Transition metal complexes of 12- membered tetraaza [N₄]and 15- membered triazadithia[N₃S₂]macrocyclic ligands: Synthetic and spectroscopic aspects.

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Abstract:

The macrocyclic ligands, 2,3,5,8,9,11hexamethyl-1,4,7,10-tetraazacyclododeca-1,3,7,9 tetraene (DADAP) and (4,5:10,11) Dibenzo(e,k)-2,13-dimethyl-3,12-diaza-6,9-dithiobicyclo(13,3,1)octadecenel-(18),2,12,14,16-pentaene (DBMAS) were synthesized and used to react with transition metal ions to synthesized the complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Pd(II). which were characterized by using elemental analysis, molar conductance, magnetic susceptibility measurements, i.r., electronic, and e.p.r. spectral studies. Spectral analyses propose octahedral stereochemical environment around Cr(III), Mn(II) and Co(II), square-planar for Ni(II) and Pd(II), and tetragonal stereochemical environment around Cu(II) with DADAP. Whereas the complexes of DBMAS ligand have a six-coordinate octahedral structures and are of a high spin kind.

Introduction:

In recent years, a key field of research has developed around the synthesis and characterization of coordination molecules with aza macrocyclic ligands [1,2]. Aza-type ligands are considered as chelating systems in the relevant literature [3, 4] and seem to be particularly promising for catalysis. For many essential biological processes, like as photosynthesis and the transportation of oxygen in mammalian and other respiratory systems, nature prefers macrocyclic derivatives.[5] The size of the macrocyclic ring has a significant impact on the ability of polyaza macrocycles to complex [6]. In electrochemically aided reactions with a variety of substrates, aza-macrocyclic ligands, as well as their coordination and organometallic compounds, play significant roles in catalytically activating small molecules [7,8]. In this study, we describe the synthesis and characterization of 2,3,5,8,9,11 hexamethyl-1,4,7,10 tetraazacyclododeca- 1,3,7,9 tetraene (DADAP) and a 15-membered [N3S2] ligands and their complexes with chromium(III), manganese(II), cobalt(II),nickel(II),copper(II), and palladium(II).

Experimental

Physical measurements

The chemicals utilized were all of the highest quality. Spectroscopic grade DMSO was utilized for the spectral and molar conductance studies. Using a Carlo-Erba 1106 elemental analyzer, C, H, and N were examined. Using Perkin-Elmer 137 equipment, IR spectra were captured in KBr. On a Shimadzu UV mini-1240 spectrophotometer, electronic spectra were captured in DMSO. On an ELICO Conductivity Bridge (CM82T), molar conductance was measured. Using CuSO4_5H2O as a calibrant, magnetic susceptibility measurements were performed at room temperature on a Gouy balance. On an E4-e.p.r. spectrometer employing the DPPH as the g-marker, the complexes' e.p.r. spectra are captured as powder samples at room temperature.

Synthesis of ligand (DADAP)

Concentrated (37%) HCl was added to an EtOH solution (20 cm³) containing 1,2-diaminopropane (0.148 g, 0.002 mol). after the solution was cooled to around 5°C, 2,3-butanedione (diacetyl) (0.172 g, 0.002 mol) was added (scheme 1.), and the mixture was refluxed for 6 hours and the resulting solid

was washed with ethanol, yield of 27% was obtained. (Found: C 67.9, H 9.4, and N 22.4; C 14H24N4; calculated: C67.7 H 9.7, and N 22.6; m.p. 132-134°C.)
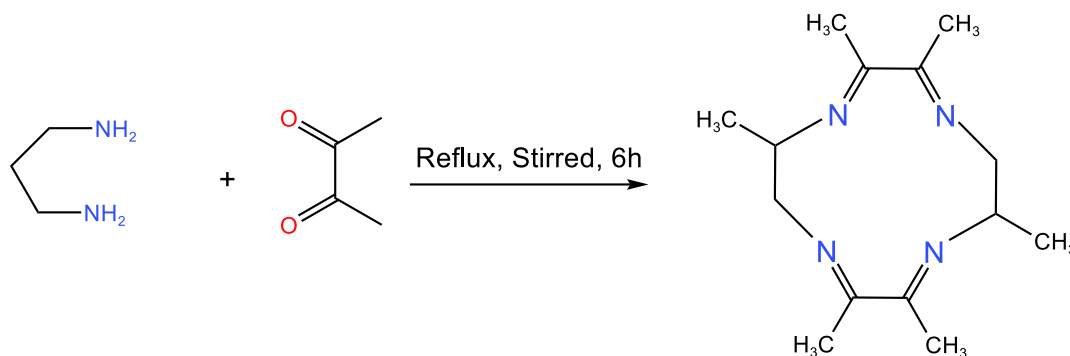
Scheme 1.

Synthesis of ligand (DBMAS)

A solution of 1,2-di(o-aminophenylthio)ethane (4.14 g, 15 mmol) in absolute EtOH (50 cm^3) was slowly added to a boiling solution of 2,6-diacetylpyridine (2.44 g, 15 mmol) in absolute EtOH (50 cm^3) with constant stirring. The mixture was then boiled under reflux for 1 hour with a few drops of conc. HCl. After cooling, a solid cream product formed, which was filtered off, washed with cold EtOH, and dried over P4O10 while under vacuum. (Yield: 80%) m.p. 178°C (Found: C, 68.5; H, 5.0; N, 10.3; C23H21N3S2 calcd.: C, 68.6; H, 5.0; N, 10.4%). Scheme 2. shows the synthetic plan.
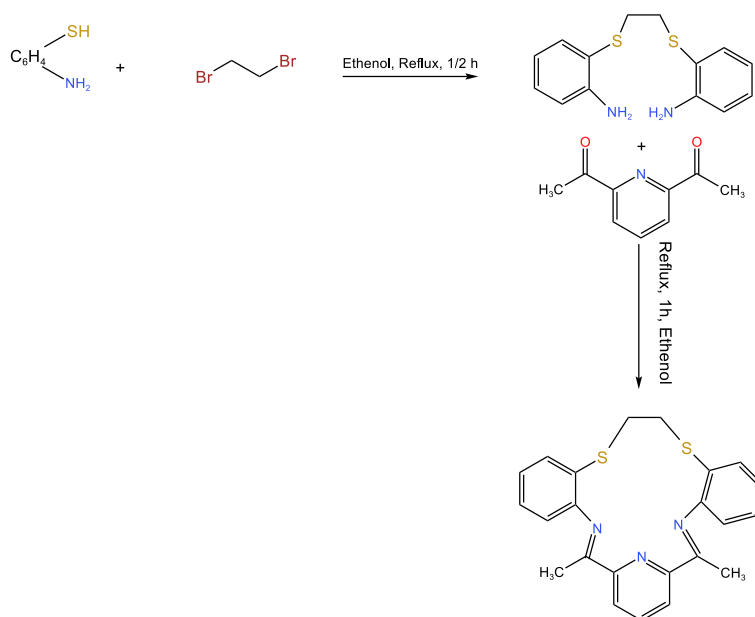
Scheme 2.

Synthesis of complexes with DADAP

Since the ligand yield is so low, the template approach was used to prepare all of the complexes. Concentrated (37%) HCl (0.002 mol) was added to an EtOH solution (20 cm^3) containing 1,2-diaminopropane (0.148 g, 0.002 mol). After the liquid had cooled to around 5°C, 2,3-butanedione (diacetyl) (0.172 g, 0.002 mol) was added, and the mixture was stirred for 30 minutes before being left to stand at room temperature. The orange solution was then mixed with an EtOH solution of the

corresponding metal salt (0.001 mol), stirred for 4–7 hours, and the colored precipitate was then washed with EtOH and dried over silica gel. In DMSO, the complexes were discovered to be soluble.

Synthesis of complexes with DBMAS

An EtOH solution of the hydrated metal chloride (1.5 mmol) was slowly added with stirring to a boiling solution of the ligand (0.603 g, approximately 1.5 mmol) in EtOH (20 cm^3). Based on the type of chloride employed, the mixture was refluxed for a specific amount of time. The colorful complexes that were produced were filtered, washed with cold EtOH, and vacuum-dried on P4O10.

Table 1. Molar conductance and elemental analysis data of the complexes

Complexes	Yield %	Mol.Cond. Ω^{-1} cm^2 mol^{-1}	colour	Found (Calcd.) %			
				C	H	N	M
[Cr(DADAP)Cl2]Cl CrC14H24N4Cl3	60	87	Green	41.1 (41.4)	5.65 (5.90)	13.2 (13.8)	12.3 (12.8)
[Mn(DADAP)Cl2 MnC14H24N4Cl2	72	10	Light brown	44.65 (44.90)	6.3 (6.4)	14.8 (15.0)	14.4 (14.7)
[Co(DADAP)Cl2] CoC14H24N4Cl2	68	15	Brown	44.3 (44.4)	6.1 (6.35)	14.7 (14.8)	15.3 (15.7)
[Ni(DADAP)]Cl2 NiC14H24N4Cl2	58	232	Light green	44.3 (44.5)	6.2 (6.3)	14.7 (14.8)	15.3 (15.3)
[Cu(DADAP)Cl2] CuC14H24N4Cl2	62	15.5	Light blue	43.7 (43.9)	6.2 (6.3)	14.4 (14.6)	16.4 (16.6)
[Pd(DADAP)]Cl2 PdC14H24N4Cl2	55	250	Green	39.3 (39.5)	5.4 (5.6)	13.0 (13.2)	24.8 (25.0)
[Cr(DBMAS)Cl]Cl2 CrC23N3S2H21Cl3	70	248	Green	60.7 (60.8)	4.4 (4.4)	9.4 (9.2)	11.6 (11.4)
[Mn(DBMAS)Cl]Cl MnC23N3S2H21Cl2	63	12	Grey	60.3 (60.4)	4.3 (4.3)	9.2 (9.2)	12.1 (12.0)
[Fe(DBMAS)Cl]Cl2 FeC23N3S2H21Cl3	65	245	Black	60.3 (60.4)	4.4 (4.3)	9.3 (9.2)	12.1 (12.2)
[Co(DBMAS)Cl]Cl CoC23N3S2H21Cl2	62	15	Black	59.8 (59.7)	4.4 (4.3)	9.2 (9.1)	12.9 (13.0)
[Ni(DBMAS)Cl]Cl NiC23N3S2H21Cl2	58	10	Blue	59.8 (59.9)	4.4 (4.3)	9.2 (9.1)	12.8 (12.7)
[Cu(DBMAS)Cl]Cl CuC23N3S2H21Cl2	76	12	Black	59.3 (59.3)	4.2 (4.3)	9.1 (9.0)	13.5 (13.6)

DADAP = 2,3,5,8,9,11hexamethyl-1,4,7,10-tetraazacyclododeca-1,3,7,9 tetraene

DBMAS = (4,5:10,11) Dibenzo(e,k)-2,13-dimethyl-3,12-diaza-6,9- dithiobicyclo(13,3,1)octadecenel-(18),2,12,14,16-pentaene.

Table 2. Electronic and e.p.r. spectral data of the complexes

Complexes	μeff.(B.M.)	λmax (cm^{-1})	giso
[Cr(DADAP)Cl2]Cl	3.72	18630,22340.25190,28810	1.98
[Mn(DADAP)Cl2]	5.91	17800,24900,28700,31650	2.01
[Co(DADAP)Cl2]	4.91	8772,18519	2.67
[Ni(DADAP)]Cl2	Diamagnetic	15000,23500	-
[Cu(DADAP)Cl2]	1.98	14085,16000	2.17
[Pd(DADAP)]Cl2	Diamagnetic	21950,25915	-
[Cr(DBMAS)Cl]Cl2	3.83	11236,18622,24038,25125	2.15
[Mn(DBMAS)Cl]Cl	5.94	11013,31446,31250,37878	2.01
[Fe(DBMAS)Cl]Cl2	5.96	15723,32467,38168	-
[Co(DBMAS)Cl]Cl	4.86	11450,14947,18656	
[Ni(DBMAS)Cl]Cl	2.98	11001,14970,18622,32051,38910	-
[Cu(DBMAS)Cl]Cl	1.89	9671,16077,31446	2.77

Table 3. Ligand field parameters of the complexes

Complexes	Dq (cm^{-1})	B (cm^{-1})	β	LFSE (kjmol^{-1})
[Cr(DADAP)Cl2]Cl	2234	330.0	0.36	320.29
[Mn(DADAP)Cl2]	1780	551.0	0.70	-
[Co(DADAP)Cl2]	1048	699.9	0.62	225.37
[Cr(DBMAS)Cl]Cl2	1862	502.8	0.542	267
[Mn(DBMAS)Cl]Cl	284	946.8	0.97	-
[Co(DBMAS)Cl]Cl	1272	848	0.75	121.57
[Ni(DBMAS)Cl]Cl	1101	934.5	0.89	157.84

Results and discussion

The complexes were given the composition listed in Table 1 based on elemental analysis. The complexes with DADAP ligand were found to have molar conductance measurements that were correspond to 1:1 electrolyte for the complexes with Cr(III), Mn(II), Co(II), and Cu(II) metal ions and 1:2 electrolyte for the complexes with Ni(II) and Pd(II) metal ions. Moreover DBMAS complexes of Mn(II), Co(II), Ni(II), and Cu(II) were 1:1 electrolytes whereas the complexes of Cr(III) and Fe(III) were 1:2 electrolytes. .In the i.r spectrum of DADAP ligand the absence of a band at about 3400 cm^{-1} indicates the absence of free amino groups. The absence of a band at 1700 cm^{-1} denotes the removal of a water molecule from the ligand. In the complexes, a new band for the C=N group that was previously identified at 1620 cm^{-1} has been moved to a lower frequency (1560–1590 cm^{-1}, demonstrating that coordination occurs through the nitrogen of the C=N group [9]. The ligand is tetradentate as a result. No band was seen for the free carbonyl group or primary amino group in ir spectrum of DBMAS, showing complete condensation had taken place. In the i.r. spectra of complexes with DBMAS ligand exhibit a moderate intensity absorption in the 1600–1700 cm^{-1} region attributable to the imine C=N group [10]. The complexes appear to be of the high-spin type based on the magnetic moments. The two highest energy pyridine ring vibrations are expected to produce medium-to-strong bands at about 1580 and 1480 cm^{-1}, which are present in all of the spectra. The 420–610 cm^{-1} range of low frequency pyridine modes [11] points to coordination of the pyridine ring. The complexes are the high-spin variety, according to the magnetic moments.

Complex of chromium(III)

Measurements of molar conductance in DMSO reveal that the complex of DADAP ligand is a 1:1 electrolyte, whereas the complex of DBAMS is 1:2 electrolyte As a result, the general composition may be represented as $[CrLCl_2]Cl$ and $[CrLCl]Cl2$ respectively. This complex has a magnetic moment (Table 2) that is near to the spin-only value and corresponds to three unpaired electrons (i.e., 3.72-3.83 B.M.). This suggests that the chromium ion is surrounded by an octahedral geometry [12]. Four bands are visible in the electronic spectra of complex of DADAP ligand, which was recorded in DMSO, and they are located at 18,630 cm^{-1} 22, 340 cm^{-1} 25, 190 cm^{-1}, and 28,810 cm^{-1} (Table 2). Three spin-allowed bands with the greatest energy band corresponding to the $^4A_{2g} \rightarrow^4 T_{1g}(P)$ transition occurring above 30,000 cm^{-1} are visible in the six-coordinate complex with Oh symmetry. Since there are four bands in the spectrum below 30,000 cm^{-1} it is impossible to explain it in terms of an idealized Oh symmetry. By assuming that the complex contains a lower symmetry element, it can be explained. The effective symmetry of these six-coordinate chromium complexes can be either D_{4h} or $C_{4v.}$ The orbital triplet's degeneracy was lifted in the order of increasing energy, resulting in the transitions $^4B_{1g} \rightarrow^4 E^a_g(v_1)$, $^4B_{1g} \rightarrow^4 B_{2g}(v_2)$, $^4B_{1g} \rightarrow^4 E^b_g(v_3)$ and $^4B_{1g} \rightarrow^4 A_{2g}(v_4)$ and the assumption of the effective symmetry around the metal ion of D4h. The electronic spectrum of Cr(III) complex of DBMAS ligand was recorded in DMSO displays three spin-allowed transitions at 25,125 cm^{-1} $[^4A_{2g} \rightarrow {}^4T_{1g}(P)]v3$; 24,038 cm^{-1} $[^4A_{2g} \rightarrow {}^4T_{1g} (F)]v2$; 18, 622 cm^{-1} $[^4A_{2g} \rightarrow^4T_{2g} (F)]$, v1; respectively Dq, B, and b, among other ligand field characteristics for both the complexes, have been estimated (Table 3). In case of DADAP complex because there is less electron-electron attraction in the metal complex than in the free ion, there is a greater gap between the electrons, effectively increasing the size of the orbitals. The value of b in the complex drops with increasing delocalization and is discovered to be less than one. This value was derived using the formula $\beta = B(complex)/B(free\ ion)$, where B is equal to 918 cm for free ions. The complex possesses a sizable amount of covalent character, according to the β value. The e.p.r. spectrum of chromium complex with DADAP ligand displays is isotropic (g_{iso} = 1.98). According to Owen [13], chromium(III)'s spin-orbit coupling constant can be used as a measure of metal-ligand covalency by reducing it from its free ion value of 90 $cm^{=1}$. A covalency parameter that is comparable to the nephelauxetic parameter and is defined as the ratio of the spin-orbit coupling constants for the complexes to those of the free chromium(III) ion can be created. The e.p.r. spectrum of chromium complex with DBMAS ligand was recorded using a polycrystalline sample at room temperature, and the g-value was calculated using the expression: g = 2.0023 (1) 4k/10Dq), where k is the spin orbit coupling constant for the metal ion in the complex. The g value is 2.1548.

Complex of Manganese(II)

Molar conductance tests on the manganese(II) complex of DADAP reveal that it is not an electrolyte (Table 1). As a result, it is written as $[Mn(DADAP)Cl_2]$. It displays a magnetic moment (5.91 B.M.) at room temperature, which is similar to the spin-only value (5.92 B.M.) and is equivalent to five unpaired electrons. This object's electronic spectrum (Table 2) of complex exhibits modest absorption bands that are indicative of octahedral geometry at 17,800 $cm^{-1}(v_1)$, 24, 900 $cm^{-1}(v_2)$, 28, 700 $cm^{-1}(v_3)$ and 31,650 cm^{-1} (v_4) [12]. You can label these bands as $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$, $6A_{1g} \rightarrow {}^4E_g$, ($^4G$), $^4A_{1g}(4G)$ (10B + 5C), and $^6A_{1g} \rightarrow {}^4E_g(^4D)$ (17B+ 5C) and $^6A_{1g} \rightarrow {}^4T_{1g}(^4P)$, respectively. Calculations have been made for the various ligand field parameters Dq, B, and β (Table 3). The energy due to transition $^6A_{1g} \rightarrow {}^4T_{1g}(^4P)$ (^4G) can be used to calculate the Dq value using Orgel's curve transition energies vs Dq [13]. The earlier described approach [14,15] was used to calculate parameter B. The low Racah B value of the manganese(II) chelate, 551, which is 70% lower than that of a free ion (786) and suggests a higher degree of covalency. An example of a polycrystalline sample's e.p.r. spectrum a single, broad isotropic signal with a centre around the Value of a free electron (g = 2.0023). The expansion of the spin relaxation is likely the cause of the spectrum [16]. In Complex in DMSO solution produces an e.p.r. spectrum. including six lines caused by the unpaired electrons' hyperfine interaction [17–18] with the Mn (I = 5/2) The nucleus. From low to high field, the nuclear magnetic quantum number MI that corresponds to the lines is -5/2, -3/2, -1/2, +3/2, +5/2. The manganese(II) complex of DBMAS has a magnetic moment of 5.94

B.M. at room temperature, or five unpaired electrons. At 11,013, 31,446, 31,250, and 37,878 cm-1, the electronic spectra showed four weak intensity absorption bands that may be attributed to $^6A_{1g} \rightarrow$ $^4T_{1g}(^4G)$, $6A_{1g} \rightarrow$ ^4E_g, (^4G), $^4A_{1g}(4G)$ (10B + 5C), and $^6A_{1g} \rightarrow ^4E_g(^4D)$ (17B+ 5C) and $^6A_{1g} \rightarrow ^4T_{1g}(^4P)$, respectively. The transitions $^6A_{1g} \rightarrow ^4E_g$ (^4D), $^4A_{1g}$ (^4G), and $^6A_{1g} \rightarrow ^4E_g$ (^4D) were used to compute the B and C values. This is because only the parameters B and C are reliant on these two transitions' energies, which are independent of the crystal field splitting energy. 946.8 and 4356.4 cm-1, respectively, are the B and C The curve transition energy versus Dq provided by Orgel can be used to calculate the value of the parameter Dq by utilizing an energy level resulting from the transition $^6A_{1g} \rightarrow$ $^4T_{1g}$. The transitions $6A_{1g} \rightarrow 4Eg$, $4A_{1g}(4G)$, and $6A_{1g} \rightarrow 4Eg(4D)$ cannot be used to determine the value of the Dq parameter since they have practically zero slope and are therefore independent of the Dq value. Table 3 provides the values of each ligand parameter. A polycrystalline sample's e.p.r. spectrum exhibits a single, broad isotropic signal with a centre value of 2.0155, or roughly the free electron g-value (g0 = 2.0023). Spin relaxation is the cause of the spectrum's enlargement [19].values.

Complex of cobalt (II)

The complex of DADAP is likewise a non-electrolyte, according to molar conductance experiments (Table 1). As a result, it might be written as [Co(DADAP)Cl₂]. At ambient temperature, it exhibits a magnetic moment of 4.91 B.M. (Table 2), a value consistent with a high-spin configuration indicating the presence of a deformed octahedral environment around the cobalt(II) ion in the complex. Absorption bands are visible in the complex's electronic spectra (Table 2) at 8772 and 18,519 cm^{-1}. Electronic spectrum analysis of this compound reveals that it has distorted octahedral geometry and may contain D_{4h} symmetry [20–21]. The spectral bands may be assigned as $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (v_1), and $^4T_{1g}(F) \rightarrow$ $^4A_{2g}(F)$ (v_3) respectively. An intra-ligand charge-transfer may have caused the band above 30,000 cm1) to form. The v_2 band, which corresponds to the $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transition and the v1 band overlap. According to Lever [21], the complex's ligand-field parameters v_3/v_1, Dq/B, B, and β have been determined (Table 3). The complex's e.p.r. spectrum was recorded at liquid nitrogen temperature since the cobalt(II)'s quick spin-lattice relaxation at higher temperatures (g∥ = 3 012 and g⊥ = 2 504) widened the lines. The significant angular orbital contribution is the cause of the g values' substantial departure from the free electron value, which is g = 2.0023.

The cobalt(II) complex of DBMAS shows magnetic moment at room temperature is 4.86 B.M. Bands at 10,500, 14,947, and 18,656 cm^{-1} are visible in its electronic spectrum. Thus, the spectra may have D_{4h} symmetry and are similar to those of complexes with deformed octahedral geometry [22-24]. Assuming that the effective symmetry is D_{4h}, different bands can be attributed to the transitions $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (v_1), $4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ (v_3), and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ respectively. Table 3 lists the complex's ligand field properties that have been calculated. The nephelauxetic value β suggests this compound has a sizable amount of covalent character. The e.p.r. spectrum was recorded at the temperature of liquid nitrogen. The expanded lines are at a higher temperature (g∥ = 4.8195 and g⊥ = 2.547) due to the quick spin lattice relaxation of cobalt(II). The significant contribution of angular momentum accounts for the greater departure of the g-values from the spin only value (g = 2.0023).

Complex of Nickel(II)

Molar conductance tests on the nickel(II) complex of DADAP ligand reveal that it is a 1:2 electrolyte (Table 1). It can be made as [Ni(DADAP)]Cl₂, and the diamagnetic properties are demonstrated by the moment of magnetism (Table 2). This suggests that the complex's geometry is square-planar. The two prominent bands at 15,000 and 23,500 cm^{-1} in its electronic spectra (Table 2) are in agreement with the reported values for square-planar nickel(II) complexes [25-26]. These bands could be attributed to the transitions $^1B_{1g} \rightarrow ^1TB_{2g}(v_1)$ and $1B_{1g} \rightarrow ^1E_g(v_3)$, respectively.

At room temperature, the complex of DBMAS exhibits a 2.98 B.M. magnetic moment. Three spin-allowed transitions, corresponding to $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$; $^3A_{2g}(F) \rightarrow ^4T_{1g}(F)$, and $^3A_{2g}$ $(F) \rightarrow ^3T_{1g}(P)$, are

seen in the electronic spectra of the nickel(II) complex at 11,001, 14,970, and 32,501(cm^{-1}). The complex possesses octahedral geometry and may have D_{4h} symmetry, according to analyses of these bands [27–29]. Several ligand field metrics show this compound to have a significant amount of covalent character.

Complex of copper (II)

According to molar conductance measurements, the complex (Table 1) can be formed as [Cu(DADAP)Cl$_2$] and is not an electrolyte. The complex's magnetic moment is 1.98 B.M. (Table 2). The D_{4h} or C_{4v} symmetry of the six-coordinate copper(II) complexes causes the E_g and T_{2g} levels of the ^2D free ion to split into the B_{1g}, A_{1g}, B_{2g}, and E_g levels, respectively. Three spin-allowed transitions are therefore anticipated in the visible and near-infrared regions, although there are currently very few complexes that have such resolved bands [24,25]. In order of increasing energy, these bands have been attributed to the following transitions: $^2B_{1g} \rightarrow ^2A_{1g}$ (dx^2-y^2 $\leftarrow$ dz^2), $^2B_{1g} \rightarrow ^2B_{2g}$ (dx^2-y^2 $\leftarrow$ dxy) and $^2B_{1g} \rightarrow ^2E_g$ (dx^2-y^2 $\leftarrow$ dxz,yz). The degree of tetragonal distortion brought on by ligand-field and Jahn-Teller processes will determine the energy level sequence [26–28]. The complex's electronic spectrum (Table 2) reveals a band at 14,085 cm^{-1} and a distinct shoulder at 16,000 cm^{-1} that can be attributed to the $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_g$ Using examples, respectively. The current complex's e.p.r. spectrum [30-31] shows well-resolved anisotropic signals in the parallel and perpendicular region. The observed data demonstrate that the values of $g_{\parallel}$ and $g_{\perp}$ are closer to 2 and $g_{\parallel} > g_{\perp}$ with $g_{\parallel}$ = 2.36 and $g_{\perp}$ = 2:08. This shows that the copper(II) complex has significant deformation from Oh symmetry.

At room temperature, the magnetic moment of the DBMAS complex is 1.89 B.M., or correspond to one unpaired electron. One may say that the complex has tetragonal geometry. The E_g and T_{2g} levels of the ^2D free ion will split into B_{1g}, A_{1g}, B_{2g}, and E_g levels, respectively, depending on the electronic symmetry of the six coordinate copper(II) complex, which has either D_{4h} or C_{4V} symmetry. In the visible and near i.r. region, three spin-allowed transitions are therefore anticipated. However, there are only a small number of complexes [32] known in which such bands are either resolved by "Gaussian Analysis" or "Single Crystal Polarization studies." The following transitions, in order of increasing energy, have been given these bands. $^2B_{1g} \rightarrow ^2A_{1g}$ (dx^2-y^2 $\leftarrow$ dz^2), $^2B_{1g} \rightarrow ^2B_{2g}$ (dx^2-y^2 $\leftarrow$ dxy) and $^2B_{1g} \rightarrow ^2E_g$ (dx^2-y^2 $\leftarrow$ dxz,yz). The amount of tetragonal distortion brought on by the ligand field and Jahn-Teller effect will determine the energy level sequence [33]. The complex has bands at 9671, 16,077, and 31,446 cm^{-1} in its electronic spectrum. The compound displays a tetragonal copper-specific anisotropic e.s.r. spectrum. G-values of 2.1769 and 2.0637 have been observed. The anisotropic g-values have been determined using Kneubuhl's techniques[34] and older methods[35]. The copper(II) complex in solution exhibits no change in its e.p.r. spectrum. It has been determined that the exchange interaction between the copper centres in a polycrystalline solid is measured by G = (g$_{\parallel}$- 2)/(g$_{\perp}$- 2). Hathaway [36-37] claims that the exchange interaction is minimal if G > 4. Significant exchange interaction in the solid complexes is indicated by a value of G< 4. There is a significant exchange interaction between the complex molecules in the complex under study because G = 2.77.

Complex of palladium (II)

The compound is a 1:2 electrolyte, according to tests of molar conductance (Table 1). Its magnetic moment revealed that it was diamagnetic (Table 2). Positive confirmation of the existence of square-planar geometry is provided by the complex's electronic spectrum [38-39]. It is possible to attribute the electronic spectral bands seen at 21,950 cm^{-1} in the palladium(II) complex to the $^1B_{1g} \rightarrow ^1A_{1g}$ transition. Charge-transfer is responsible for other electronic spectral bands that emerge at 25,915 cm-1 and above. It is possible to determine the value of Δ from the first spin permitted d-d transition by assuming that the Slater-Condon inter-electronic repulsion parameters have a value of F2 = 10F4 = 600 [40].

Complex of Iron (III)

Iron(III) complex has a 5.96 B.M. magnetic moment at ambient temperature. Bands are visible in the complex at 15,723, 32,467, and 38,168 cm^{-1}[41] It is highly improbable that the spectra of the iron(III) derivatives, which are more covalent than those of manganese(II), can be explained in terms of very specific values of B and C.
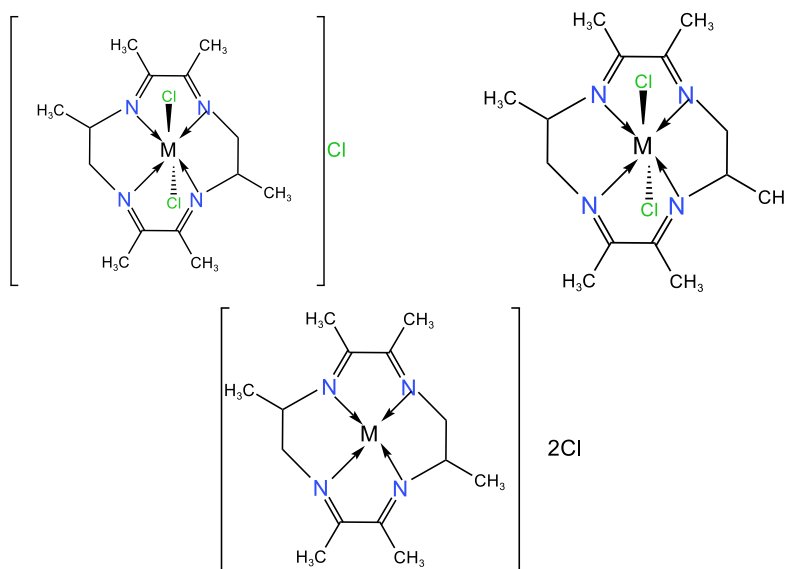
M = Cr(III), L = DADAP   M = Mn(II). Co(II), L = DADAP   M= Ni(II), Pd(II), L = DADAP
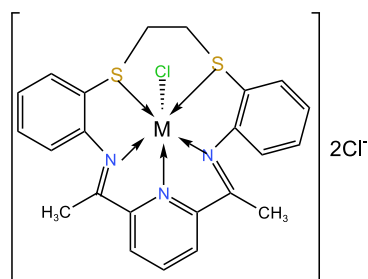
M = Cr(III), Fe(III), L = DBMAS   M = Mn(II), Co(II), Ni(II), Cu(II), L = DBMAS

Scheme 3. Proposed Structures of the synthesized complexes.

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