Magnetic and Spectroscopic Studies on Dimeric Cobalt(II) Complexes of the Tetradentate Ligand (4,5-Dimethyl-3-pyrazolyl)aldazine

ALI EL-DISSOUKY* and G. B. MOHAMAD

Chemistry Departments, Faculties of Science and Education, Alexandria University, Alexandria (Egypt)

(Received November 14, 1988; revised March 21, 1989)

Abstract

Infrared, electronic and electron spin resonance spectral studies together with the molar conductivity and variable temperature magnetic susceptibility data are presented for cobalt(II) complexes of the types: (a) $[CoXL]X \cdot \frac{1}{2}H_2O$, (b) $[Co_2X_3L]X \cdot nH_2O$ and (c) $[Co_2X_4L_2] \cdot H_2O$, X = Cl or Br and $n = \frac{1}{2}$ or 1 and L = (4,5-dimethyl-3-pyrazolyl)aldazine. The formulations are based on elemental analysis and molar conductivity data. Infrared and electronic spectral results show that cobalt(II) complexes are trigonal bipyramidal, tetrahedral and octahedral structures for (a), (b) and (c), respectively. The variable temperature magnetic susceptibility data indicate a weak antiferromagnetic interaction in all complexes. The parameters, J, g, K^2, Dq and B' are calculated and rationalized in terms of the electronegativity of the coordinated halides and the geometrical shapes. The dimeric nature of class (a) compounds is further substantiated by the complexity of their ESR spectra at 4.8 K.

Introduction

Potentially binucleating ligands are important in model studies of metalloproteins containing two metal ions in close proximity. Examples of these ligands are diazines, pyridazines, hydrazines and phthazines [1–10]. These ligands form complexes with antiferromagnetic exchange between the two metal centers via bridging ligands [1–5]. The binucleating ligand, 2-pyridinealdazine (PAA) investigated by Stratton and Busch [9], was an early example of a system involving a two azine bridge. Our interest in biologically active substituted hydrazines and hydrazones [11–20], rests with their potential to form mononuclear and binuclear metal complexes with various stereochemistries and magnetic properties. In this report we describe the

synthesis and characterization of binuclear cobalt(II) complexes of the new chelating agent, (4,5-dimethyl-3-pyrazolyl)aldazine, L, by various physical techniques.

Experimental

All reagents used were purchased from commercial sources and used without further purifications, but all solvents were dried prior to use.

Electronic spectra were recorded with a Cary 17 spectrophotometer. Infrared spectra were obtained as KBr discs with a Pye Unicam SP3-300 spectrophotometer. Magnetic susceptibilities were measured by the Faraday method as described before [11–15]. Molar conductivities were carried out in a Systronics (303 model) direct reading conductivity meter. ESR spectra were obtained as previously reported [11–14]. Carbon, hydrogen, nitrogen and halogen contents in each complex were performed by the Mikroanalytisches Labor Paschen, Busch-Str. 54 Bonn 1, F.R.G. Cobalt analysis was obtained by using standard complexometric titration [21]. The elemental analyses are given in Table 1.

Preparation of Cobalt(II) Complexes

$[Co_2X_3L]X \cdot nH_2O$, X = Cl or Br and $n = \frac{1}{2}$ or 1
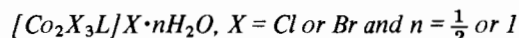
The chelating agent (0.01 mol) was dissolved in dry absolute EtOH–triethylorthoformate (10:1 vol./vol.) (30 ml) and added under pure N_2 to a deaerated solution of the corresponding cobalt(II) halide (0.022 mol) in the same solvent (20 ml). The reaction mixture was stirred at room temperature for 4–5 h and the solid precipitate was filtered off, recrystallized from dry absolute EtOH and dried in a vacuum desiccator.

$[Co_2X_4L_2] \cdot H_2O$, X = Cl or Br
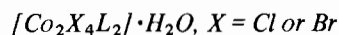
These compounds were prepared as described for $[Co_2X_3L]X \cdot nH_2O$ but in mole ratio 1:1 (Co:L) under heating at 50–60 °C for 3–4 h. If the temperature was raised higher, contaminated unknown products were obtained.

---

*Present address: Chemistry Department, Faculty of Science, United Arab Emirates University, Al-Ain, P.O. Box 15551, U.A.E.

TABLE 1. Analytical data, room temperature magnetic moments (BM) and some physical properties

Compound	Colour	μ_{eff} (298)	Λ_M [a]	Analytical data: found (calc.) (%)				
				C	H	N	Co	X
$[CoClL]Cl \cdot \frac{1}{2}H_2O$	brown	4.38	47.02	37.08 (37.60)	4.44 (4.44)	22.00 (21.94)	15.28 (15.39)	18.54 (18.54)
$[CoBrL]Br \cdot \frac{1}{2}H_2O$	brown	4.22	50.36	30.26 (30.51)	3.57 (3.60)	17.63 (17.79)	12.54 (12.49)	34.00 (33.90)
$[Co_2Cl_3L]Cl \cdot H_2O$	olive green	4.28	20.19	27.19 (27.59)	3.40 (3.45)	16.00 (16.09)	22.39 (22.58)	27.35 (27.21)
$[Co_2Br_3L]Br \cdot \frac{1}{2}H_2O$	green	4.26	26.30	20.53 (20.81)	2.50 (2.46)	11.99 (12.14)	16.92 (17.03)	46.00 (46.35)
$[Co_2Cl_4L_2] \cdot H_2O$	green	4.54	1.38	37.35 (37.60)	4.40 (4.44)	21.98 (21.94)	15.28 (15.39)	18.70 (18.54)
$[Co_2Br_4L_2] \cdot H_2O$	olive green	4.47	2.00	30.16 (30.51)	3.62 (3.60)	17.88 (17.79)	12.56 (12.49)	34.08 (33.96)

[a]Molar conductivity of 10^{-3} M solutions in nitrobenzene at 25 °C.

$[CoXL]X \cdot \frac{1}{2}H_2O$, X = Cl or Br

A solution of the chelating agent (0.01 mol) in absolute EtOH−triethylorthoformate (10:1 vol./vol.) (30 ml) was added to a deaerated solution of the corresponding cobalt(II) halide (0.01 mol) in the same solvent (25 ml) while passing of pure N_2. The reaction mixture was stirred for 5 min at room temperature. The crystalline solid formed was filtered off, washed several times with EtOH and dried in a vacuum desiccator.
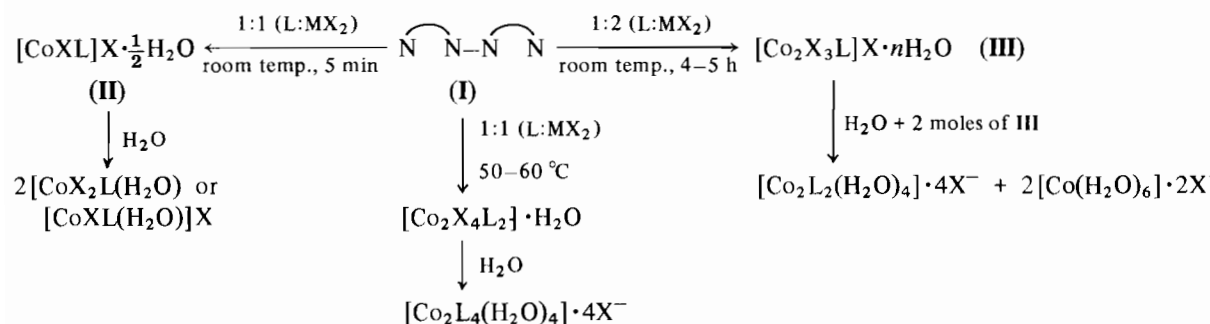
Results and Discussion

It was found that the presence of water in the solvents used in the preparation of the complexes leads to formation of unknown mixtures with a source of hydrolysis with the formation of the parent aldehyde and hydrazine. This could be attributed to the unstability of this azine compound in the presence of water and metal ion although it is very stable in the presence of water. This could be explained according to Woon et al. [10], in terms of an enhancement of the electrophilic nature

of the azomethine center during coordination of an azine nitrogen to cobalt(II) ion which in turn enhances nucleophilic attack at this center by water. To prevent this hydrolysis, dry pure EtOH−triethylorthoformate mixture was used to minimize or eliminate water. The complexes are soluble in most organic solvents but water leads to their disproportionation and/or replacement of the coordinated halides by water molecules as confirmed from their electronic spectra. The synthetic Scheme 1, utilized in this article could be assumed.

The molar conductivities of 10^{-3} M solutions in $PhNO_2$ at 25 ± 1 °C, Table 1, indicate the 1:2, 1:1 and non-electrolytic natures of class (a), (b) and (c) compounds [22], respectively.

Infrared Spectra

The main IR bands of the ligand and its cobalt(II) complexes are given in Table 2. The medium broad band centered at 3320 cm^{-1} and the weak one at 1682 cm^{-1} due to $\nu(NH)$ and $\delta(NH)$, respectively in the spectrum of the free ligand have been slightly shifted to lower wavenumbers in all complexes. The bands at 1642 and 1546 cm^{-1} in the spectrum

Scheme 1.

TABLE 2. Main IR spectral bands (cm^{-1})

Compound	ν(NH)	ν(C=N) Pz	ν(N-N) Pz	ν(C=N) azine	δ ring	ν(Co-N) Pz	ν(Co-N) azine	ν(N-N) azine
L	3320	1546	1018	1642	654			988
[CoClL]Cl·$\frac{1}{2}$H$_2$O	3280	1572	1036	1634 1556	672	326	490	1012
[CoBrL]Br·$\frac{1}{2}$H$_2$O	3298	1569	1030	1636 1552	676	328	492	1015
[Co$_2$Cl$_3$L]Cl·H$_2$O	3216	1568	1036	1616	672	334	522	1022
[Co$_2$Br$_3$L]Br·$\frac{1}{2}$H$_2$O	3220	1572	1038	1618	668	336	526	1020
[Co$_2$Cl$_4$L$_2$]·H$_2$O	3222	1578	1036	1620	668	322	516	1024
[Co$_2$Br$_4$L$_2$]·H$_2$O	3228	1580	1032	1622	668	320	518	1022

of the free ligand are assigned to ν(C=N) of the azine and pyrazole (Pz), respectively. ν(C=N)$_{Pz}$ exhibits a positive shift (c. 32–22 cm^{-1}) upon complexation indicating the bonding of pyrazole-N^2 to cobalt(II). This was supported by the blue shifts of ν(N-N)$_{Pz}$ from 1018 cm^{-1} in the free ligand to 1030–1038 cm^{-1} in the complexes and the band due to the in-plane pyrazole ring by 14–22 cm^{-1}. The band at 1642 cm^{-1} was found to be sensitive to the stoichiometry of the complexes. The spectra of [CoXL]X·$\frac{1}{2}$H$_2$O, X = Cl or Br, display two bands at 1634–1636 and 1552–1556 cm^{-1} which could be assigned to ν(C=N)$_{azine}$. This suggests that the two C=N groups are not identical in these compounds. The band at 1552–1556 cm^{-1} agrees with the presence of a five-membered chelate ring [9, 23] and that at 1634–1636 cm^{-1} due to the involvement of the second C=N in a six-membered chelate ring. The small shift of this band indicates that the conjugative effects of a six-membered chelate ring are more limited and does not greatly change the vibration of the C=N group [9]. Accordingly L can act as tridentate in these compounds, structure Ia. The spectra of [Co$_2$X$_3$L]X·nH$_2$O, X = Cl or Br and $n = \frac{1}{2}$ or 1, exhibit a new medium to strong band at 1616–1622 cm^{-1} with the disappearance of that at 1642 cm^{-1}. This band could be assigned to ν(C=N)$_{azine}$ and further indicates that the formation of two similar five-membered chelate rings. The disappearance of the band at 1642 cm^{-1} could be attributed to the cobalt–L–π-electron interaction in the five-membered chelate rings leading to a great change in ν(C=N). The far IR spectra of [Co$_2$X$_4$L$_2$]·H$_2$O, X = Cl or Br, gave similar results as for the 1:2 (L:M) class. The spectra of all complexes exhibit bands at 320–336 and 490–526 cm^{-1} which are not present in the spectrum of L and assigned to ν(Co-N) of pyrazole-N^2 and azine, respectively [17–20]. It is interesting to mention that ν(Co-N)$_{azine}$ in classes (b) and (c) are at a higher wavenumber rela-

tive to that of class (a) compounds indicating stronger Co-L interaction in 5,5-membered chelate rings than in 5,6-membered chelate rings. The far IR spectra of [CoXL]X·$\frac{1}{2}$H$_2$O and [Co$_2$X$_3$L]X·nH$_2$O exhibit a medium band at 216–225 cm^{-1} due to the bridged chloride, in addition to bands at 292 and 228 cm^{-1} in the spectra of the latter due to ν(Co-Cl)$_{terminal}$ and ν(Co-Br)$_{terminal}$, respectively. The spectra of [Co$_2$X$_4$L$_2$]·H$_2$O exhibit bands at 305 and 234 cm^{-1} due to terminal ν(Co-Cl) and ν(Co-Br), respectively. The fact that the ν(Co-X) band is somewhat lower than the range reported for the terminal halides could be interpreted as a result of a Co-X...HN-Pz hydrogen bonding. The IR spectra of all complexes indicate the absence of coordinated water molecules. According to these IR data structures Ia, Ib and Ic could be assumed.

Ia

Ib

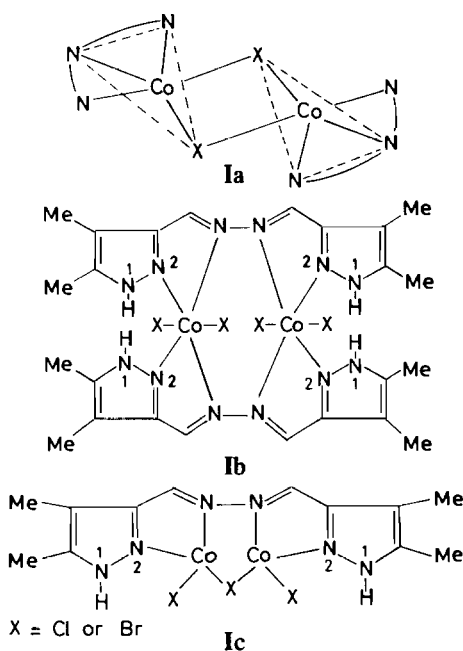Ic

X = Cl or Br

TABLE 3. Electronic spectral data (cm^{-1})

Compound	$(CH_2Cl)_2$						H_2O		
	$^4A'_2(F) \longrightarrow$						$^4T_{1g} \longrightarrow$		
	$^4E(F)$	$^4E'(F)$	$^4A'_2(P)$	$^4E(P)$	Dq	B'	$^4T_{2g}$	$^4A_{1g}$	$^4T_{1g}(P)$
$[CoClL]Cl \cdot \frac{1}{2}H_2O$	5620, 6450	13050	17400	20800	9540	792	8050	17500	18230 21300
$[CoBrL]Br \cdot \frac{1}{2}H_2O$	5560 6430	12985	17580	20580	9230	781	8400	17470	18060 20990
	$^4A_2 \longrightarrow {}^4T_1(F)$		$^4A_2 \longrightarrow {}^4T_1(P)$		Dq	B'			
$[Co_2Cl_3L]Cl \cdot H_2O$	6200, 10500	8460,	14500, 18000,	15000 18900	5000	586	8340	17480	17990 20960
$[Co_2Br_3L]Br \cdot \frac{1}{2}H_2O$	5700, 10600	7800	13950, 16600,	14400 18600	4790	573	8325	17500	18020 21000
	$^4T_{1g} \longrightarrow {}^4T_{2g} \longrightarrow {}^4A_{1g} \longrightarrow {}^4T_{1g}(P)$				Dq	B'			
$[Co_2Cl_4L_2] \cdot H_2O$	8300		17350	19000 21990	9500	786	8400	17600	18020 21000
$[Co_2Br_4L_2] \cdot H_2O$	8050		16600	18700 20890	9010	774	8390	17600	18000 21000

Electronic Spectra

The electronic spectra of all complexes either as solid reflectance or $(CH_2Cl)_2$ solutions exhibit very intense bands at 30 200–32 100 and 24 380–25 450 cm^{-1} assigned to $\pi-\pi^*$ intraligand and M–L charge transfer transitions, respectively [19, 23].

The spectra of $[Co_2X_3L]X \cdot nH_2O$ exhibit bands with shapes and positions (Table 3) characteristic of pseudo-tetrahedral cobalt(II) complexes [10–12, 24, 25]. The ligand field parameters Dq and B' are calculated [19, 25] and given in Table 3. Both Dq and B' values are found to be in the sequence Cl > Br, consistent with their electronegativities, Cl(3.0) and Br(2.8). This could be attributed to the expansion of the cobalt d-orbitals as a result of the decrease in the electronegativity of the coordinated halide ion which in turn leads to a decrease in the positive charge on cobalt(II). In aqueous solutions, the spectra of these complexes (Table 3) exhibit bands characteristic of octahedral cobalt(II). These are in addition to a band at 8130 cm^{-1} characteristic of ν_1 for $[Co(H_2O)_6]^{2+}$. This could be explained on the basis of the disproportionation of these complexes in water as given in Scheme 1.

The electronic spectra of $[Co_2X_4L_2] \cdot H_2O$, show three bands with shapes and intensities characteristic of a distorted octahedral ligand field around cobalt(II). ν_3 (Table 3) was found to be split in nature suggesting the possibility of a *trans* structure involving four coordinated nitrogen donors. Furthermore, the lower energy absorption indicate co-

ordinated halide ions. The values of Dq and B' were calculated [12, 26] (Table 3) and are consistent with those reported for distorted octahedral cobalt(II) complexes [26–28]. The spectra of these complexes as aqueous solutions, exhibit identical bands in both chloro and bromo complexes and are rather consistent with those reported for octahedral cobalt(II) complexes. Furthermore, the molar conductivity in water indicate 1:4 electrolytes. This may be taken as evidence for the replacement of the halide by water molecules, Scheme 1.

The electronic spectra of $[CoXL]X \cdot \frac{1}{2}H_2O$ (Table 3) are similar to that reported for $[CoMe_6trenCl]Cl$ in which the spectral data have been assigned on the basis of the crystal structure studies [29]. Accordingly, the following assignments can be suggested for our complexes. The bands at 5560–5620 and 6430–6470 cm^{-1} are attributed to the electronic transitions involving the $^4A_2$ ground state and the first ^4E excited level. The band at 12 985–13 050 cm^{-1} could be attributed to the transition between $^4A_2$ and the second ^4E term. The absorptions at 17 400–17 580 cm^{-1} and 20 580–20 800 cm^{-1} are assigned to $^4A_2 \rightarrow {}^4A_2(p)$ and $^4A_2 \rightarrow {}^4E(p)$ transitions, respectively in trigonal bipyramidal cobalt(II) complexes, structure **Ia** [29, 30]. In aqueous solutions, the spectra of these complexes exhibit bands (Table 3) characteristic of a pseudo-octahedral configuration around cobalt(II). The formation of octahedral species in water could be attributed to either the extension of the coordination

number of the cobalt ion in the dimer to six by coordination to water molecules and/or the dissociation and bonding to water as given in Scheme 1.

Magnetic Properties

The magnetic susceptibility data of the complexes in the temperature range 78–300 K obey the Curie–Weiss law and the values of theta were found to be in the range 63–88 K which are larger than those reported for monomeric cobalt(II) complexes. Since the electronic spectral data do not show the presence of any traces of cobalt(III), these magnetic data could be interpreted on the basis of the dimeric and partial covalent characters of these complexes.

The susceptibility data of $[CoXL]X \cdot \frac{1}{2}H_2O$ corrected for diamagnetism and for independent paramagnetism are given in Table 4. The data were least-squares fitted to eqn. (1) which is valid assuming an isotropic Weisenberg exchange in a given d^n–d^n binuclear system characterized by the spins S_1 and S_2 [31]

$$\chi_M = \frac{N\beta^2 g^2}{kT} \frac{\Sigma_s \Sigma M_s (M_s)^2 \exp^{-E(S)/KT}}{\Sigma_s \Sigma M_s \exp^{-E(S)/KT}} \qquad (1)$$

where $S = S_1 + S_2$ and $E(S) = -J/2S(S + 1) - S_1(S_1 + 1) - S_2(S_2 + 1)$ and the other symbols have their usual meanings. This formula was derived from the van Vleck equation considering the Zeeman

TABLE 4. Magnetic susceptibilities (cm^3 mol^{-1}) after correction for temperature independent paramagnetism and diamagnetism

T (K)	$10^3\chi$	μ_{eff}/Co	T (K)	$10^3\chi$	μ_{eff}/Co	T (K)	$10^3\chi$	μ_{eff}/Co
$[CoClL]Cl \cdot \frac{1}{2}H_2O$			$[Co_2Cl_3]Cl \cdot H_2O$			$[Co_2Cl_4L_2] \cdot H_2O$		
300.0	16.15	4.40	300.0	15.33	4.285	300.0	17.33	4.560
290.1	16.21	4.34	289.9	15.72	4.275	290.0	17.86	4.550
276.0	17.01	4.33	278.8	16.35	4.270	279.9	18.35	4.530
262.0	17.48	4.28	270.3	16.84	4.266	260.0	19.19	4.467
249.0	18.29	4.27	260.4	17.42	4.259	240.8	20.37	4.430
225.0	20.01	4.24	250.0	18.07	4.250	220.0	21.83	4.383
215.0	20.65	4.21	240.0	18.88	4.245	209.0	22.42	4.329
199.2	21.70	4.16	228.4	19.64	4.235	190.4	24.03	4.278
180.0	22.85	4.05	220.0	20.30	4.226	168.9	25.91	4.183
159.0	25.49	4.03	208.0	21.29	4.208	148.0	28.09	4.088
150.1	26.98	4.02	200.0	21.98	4.193	128.0	30.08	3.968
139.2	28.62	3.99	178.0	24.24	4.154	108.2	33.89	3.829
130.0	30.28	3.97	155.9	27.01	4.105	100.0	35.39	3.762
115.0	33.55	3.92	140.0	29.51	4.065	90.4	36.97	3.655
105.0	35.85	3.87	120.0	33.43	4.005	82.0	37.37	3.518
95.0	36.88	3.74	107.9	36.48	3.969	78.0	39.21	3.497
85.0	38.98	3.64	84.0	45.16	3.895			
78.0	39.88	3.52	78.0	48.17	3.876			
$[CoBrL]Br \cdot \frac{1}{2}H_2O$			$[Co_2Br_3L]Br \cdot \frac{1}{2}H_2O$			$[Co_2Br_4L_2] \cdot H_2O$		
300.0	14.91	4.23	300.0	15.16	4.265	300.0	14.63	4.189
291.2	15.27	4.21	290.1	15.65	4.260	290.0	14.95	4.164
280.0	15.66	4.18	279.9	16.19	4.258	280.1	15.39	4.151
269.1	16.07	4.16	269.0	16.83	4.255	271.0	15.87	4.147
260.0	16.45	4.14	250.0	18.04	4.247	259.9	16.18	4.102
252.1	16.91	4.13	239.5	18.77	4.240	245.9	17.01	4.090
240.0	17.42	4.09	218.0	20.52	4.230	230.0	18.05	4.074
231.0	18.01	4.07	200.0	22.26	4.220	221.8	18.67	4.069
220.0	18.64	4.05	180.0	24.47	4.197	214.0	19.16	4.049
199.0	20.03	3.99	157.9	27.46	4.165	200.0	20.19	4.018
180.1	21.15	3.93	140.0	30.17	4.110	190.0	21.10	3.995
168.1	22.72	3.91	120.0	34.40	4.063	173.9	22.47	3.954
157.1	23.89	3.87	100.0	39.43	3.971	160.0	23.81	3.903
144.8	24.69	3.78	92.0	40.96	3.882	142.0	25.59	3.840
136.9	25.69	3.75	86.0	43.10	3.850	118.0	29.41	3.725
122.0	27.72	3.68	80.0	45.13	3.800	100.0	32.68	3.615
108.1	29.86	3.59	78.0	45.27	3.758	90.0	34.96	3.547
99.9	30.76	3.51				82.0	37.04	3.485
85.9	33.53	3.40				78.0	37.81	3.434
78.0	34.53	3.28						

effect in the d^n–d^n binuclear system. The values of J and g which minimize the function, $R = (\Sigma_i(\chi_{obs} - \chi_{calc})^2/\chi_{obs}^2)^{1/2}$, are -4.84 and 5.05 cm^{-1} and 2.33 and 2.308 cm^{-1} for X = Cl and Br, respectively. The small J values could be interpreted on the basis of the angular overlap model proposed by Bencini and Gatteschi [32]. For qualitative applications of this model for cobalt(II) dimers, the unpaired electrons occupy a_g and b_u orbitals which originate from the splitting of the two d_{yz} in trigonal bipyramidal configuration, or the b_g and a_u derived from the two d_{xz} which are characterized by intermediate energy in the proposed diagram, Fig. 1. The latter level can be occupied by two electrons having parallel spins giving rise to a ferromagnetic contribution to the exchange constant J. Therefore the resulting ferromagnetic and antiferromagnetic contributions partially compensate one another and small values of J are obtained. Furthermore, the order of J values, Cl $<$ Br could be explained on the basis that the bond angle Co—X—Co is larger in the case of X = Br than in the case of X = Cl. As shown in Fig. 1, as the bond angle increases, the energy separation between the a_g and b_u orbitals increases and therefore the antiferromagnetic coupling between the two cobalt(II) ions is favoured, the exchange coupling constant, assuming a negative value.

The magnetic data for $[Co_2X_3L]X \cdot nH_2O$ given in Table 4 indicate the presence of a weak magnetic interaction. The molar paramagnetic susceptibility for an $S_1 = S_2 = 3/2$ binuclear complex is given by eqn. (2) derived from the van Vleck equation [33],

$$\chi_M = \frac{N\beta^2g^2}{3kT} \frac{42 + 15e^{6x} + 3e^{10x}}{7 + 5e^{6x} + 3e^{10x} + e^{12x}}$$
$$+ \frac{8N\beta^2K^2}{10Dq} \qquad (2)$$

where K^2 is a measure of the contribution of ligand (p-orbital) wave function to the total wave functions of the ground state of the metal atom and is, therefore, related to the molecular orbital coefficients describing this mixing and to the metal—ligand overlap integral [34]. $8N\beta^2K^2/10Dq$ represents the temperature independent paramagnetism arising from the second Zeeman effect. $x = -J/kT$ and the other terms have their usual meanings. The experimental data are fitted to eqn. (2) and the magnetic parameters which gave the best fit are given in Table 5.

The magnetic data for $[Co_2X_4L_2] \cdot H_2O$ (Table 4) are fitted to eqn. (3) and the equation given by Ball and Blake [3] in which the spin—orbit coupling effect is considered. The magnetic data which gave the best fit to both expressions are given in Table 5.
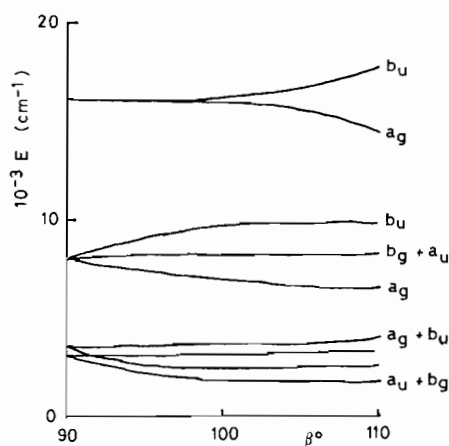

Fig. 1. Energy level diagram for five-coordinate trigonal-bipyramidal dimers showing the effect of the variation of M—X—M ($\beta°$).

TABLE 5. Magnetic parameters of cobalt(II) complexes

Compound	θK	$-J$ (cm^{-1})	g	K^2	σ^a (BM)
$[CoClL]Cl \cdot \frac{1}{2}H_2O$	-70	4.84	2.330		0.010
$[CoBrL]Br \cdot \frac{1}{2}H_2O$	-88	5.05	2.308		0.009
$[Co_2Cl_3L]Cl \cdot H_2O$	-78	3.91	2.272	0.86	0.012
$[Co_2Br_3L]Br \cdot \frac{1}{2}H_2O$	-62	4.52	2.246	0.66	0.011
$[Co_2Cl_4L_2] \cdot H_2O$	-63	6.88 (5.70)^b	2.420	0.88^b	0.006
$[Co_2Br_4L_2] \cdot H_2O$	-68	7.36 (6.34)^b	2.43	0.79^b	0.007

^{a}Standard deviation of the magnetic moment. The T.I.P. correction was calculated from the relation, T.I.P $= 2.088K^2/10Dq$. ^{b}Calculated using the model given in ref. 3.

$$\chi_M = \frac{14 + 5e^{6x} + e^{10x}}{7 + 5e^{6x} + 3e^{10x} + e^{12x}} \frac{N\beta^2g^2}{kT} \qquad (3)$$

where $x = -J/kT$ and the other symbols have their usual meanings. It can be seen that the best fit to the equation given by Ball and Blake is better than that to eqn. (3). This is because of the effect of the spin—orbit coupling on the splitting of the $^4T_{1g}$ ground state in the octahedral geometry which leads to the distortion from the idealized symmetry and therefore to the exchange interaction.

Examination of the data in Table 5 shows that: (i) there is a relatively small difference in J values between the trigonal bipyramidal $[CoXL]X \cdot \frac{1}{2}H_2O$ and the octahedral $[Co_2X_4L_2] \cdot H_2O$ complexes. This could result from two opposing factors. First when the metal ion is moved into the plane, the overlap between the $d_{x^2-y^2}$ of the cobalt(II) and the bridging ligand hybrid orbitals is increased. This

overlap represents the superexchange mechanism which leads to an increase in the antiferromagnetic interaction. Secondly, the structural changes will result in a stronger ligand field about the metal ions leading to an enhanced difference between the energies of the metal and the bridging ligand orbitals. This leads to a decrease in the exchange interaction. Therefore the two effects partially reduce each other. (ii) The J values for all complexes are in the order Br Cl, which is the reverse of their electro-negativities. This could be explained by the following: as the electronegativity of the halide ion decreases, the positive charge on the cobalt(II) decreases leading to the expansion of the cobalt(II) d-orbitals and the enhancement of the exchange. This observation is confirmed from the B' values. Furthermore, these results are reverse to the data obtained for Cr_2X_9 ($S = 3/2$), $X = Cl$ or Br, for which a direct exchange interaction mechanism was assumed [35]. Accordingly a superexchange interaction mechanism could be assumed [13, 14]. (iii) In all cases, the K^2 values are less than unity, suggesting that the chelating agent, L, is a good electron acceptor as a result of the length of the conjugated pathway and bonding of one ligand to two metal ions. This allows a greater cobalt—halogen bonding leading to reduce K^2 values. (iv) There is a good agreement between the electronic spectral (Dq, B') and magnetic (J, K^2) parameters where they exhibit a parallel trend.

Electron Spin Resonance Spectra

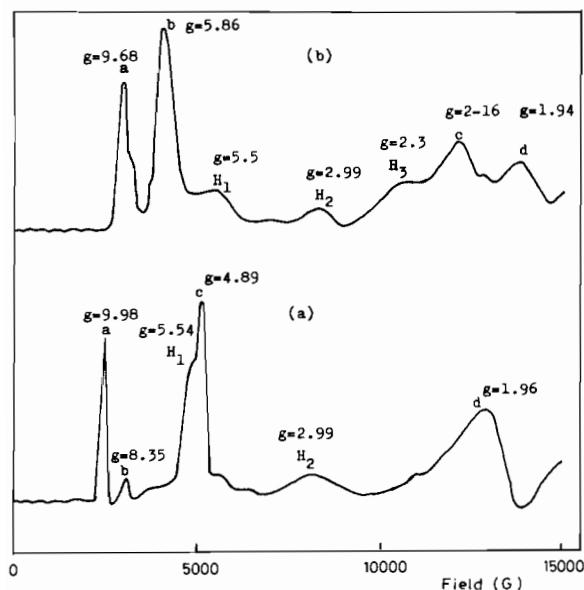The Q-band ESR spectra of the polycrystalline samples $[CoXL]X \cdot \frac{1}{2}H_2O$ at 4.8 K are shown in

Fig. 2. The spectra are complicated in nature which could be attributed to (i) the presence of exchange coupling interaction and the zero field splitting and (ii) the proximity of the metal ions leading to a large through space dipolar zero field splitting which is orientation dependent. The latter term will not be energetically large relative to the overall spread of energies encountered for the system but will split a part of the most important levels and result in obvious changes in the spectra.

The spectra of both complexes are similar showing that the average of the positions of peaks a and b are nearly the same. The splitting is larger for the bromide and if these splittings are indeed due to the dipole—dipole interactions and the g—D tensor orientation does not change, then the Co—Co distance is clearly smaller in bromide than in chloride [36]. In both spectra, the components a and b are two interior zero field split components of the $g_\perp$ transition while peak d is probably the parallel signal from the lowest manifold. The broadness of this signal could be attributed to small parallel zero field splitting. The peaks H_1 and H_2 may be due to the parallel and perpendicular components from some higher energy manifold.

Fig. 2. Q-band ESR spectra of the polycrystalline samples of (a) $[CoClL]Cl \cdot \frac{1}{2}H_2O$; (b) $[CoBrL]Br \cdot \frac{1}{2}H_2O$; at 4.8 K.

References

1 A. B. P. Lever, L. K. Thompson and W. Reiff, *Inorg. Chem., 11* (1972) 2292.
2 H. Alper, *J. Organomet. Chem., 50* (1973) 209.
3 P. W. Ball and A. B. Blake, *J. Chem. Soc., Dalton Trans.,* (1974) 852.
4 D. A. Sullivan and G. J. Palenik, *Inorg. Chem., 16* (1977) 1127.
5 J. A. Doull and L. K. Thompson, *Can. J. Chem., 58* (1980) 221.
6 J. C. Dewan and L. K. Thompson, *Can. J. Chem., 60* (1982) 12.
7 G. Bullock, F. W. Hartstock and L. K. Thompson, *Can. J. Chem., 61* (1983) 57.
8 C. J. O'Connor, R. J. Romanach, D. M. Robetson, E. E. Eduok and F. R. Fronezek, *Inorg. Chem., 22* (1983) 449.
9 W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc., 82* (1960) 4834.
10 T. C. Woon, L. K. Thompson and P. Robichaud, *Inorg. Chim. Acta, 90* (1984) 20.
11 A. El-Dissouky, S. A. El-Shazly and M. Gaafar, *Transition Met. Chem., 8* (1983) 175.
12 A. El-Dissouky and L. S. Refaat, *Inorg. Chim. Acta, 87* (1984) 213.
13 A. El-Dissouky, M. M. Abou-Sekkina and A. Z. El-Sonbati, *Transition Met. Chem., 9* (1984) 372.
14 A. El-Dissouky, *Transition Met. Chem., 9* (1984) 112.
15 A. El-Dissouky, A. M. Hindawey and A. Abdel-Salam, *Inorg. Chim. Acta, 118* (1986) 109.
16 A. El-Dissouky, A. M. Hindawey and A. Abdel-Salam, *Inorg. Chim. Acta, 119* (1986) 207.
17 A. El-Dissouky and A. Z. El-Sonbati, *Synth. React. Inorg. Met-Org. Chem., 16A* (1986) 1035.
18 A. El-Dissouky, A. Kasem and A. Z. El-Sonbati, *Transition Met. Chem., 11* (1986) 449.

19 A. El-Dissouky, A. Fahmy and A. Amer, *Inorg. Chim. Acta, 133* (1987) 311.
20 A. El-Dissouky, *Spectrochim. Acta, Part A, 43* (1987) 1117.
21 F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, Van Nostrand, Princeton, N.Y., 1965.
22 W. J. Geary, *Coord. Chem. Rev., 7* (1971) 81.
23 J. E. Andrew, P. W. Ball and A. B. Blake, *Chem. Commun.*, (1969) 143.
24 S. D. Ross, *Spectrochim. Acta, 18* (1962) 255.
25 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968.
26 A. B. P. Lever, *J. Chem. Soc. A*, (1967) 2041.
27 B. Singh and U. Agrawal. *Inorg. Chem., 8* (1969) 2341.
28 G. R. Burs, *Inorg. Chem., 7* (1968) 277.
29 I. Bertini, M. Ciampolini, P. Dapporto and D. Gatteschi, *Inorg. Chem., 11* (1972) 2254.
30 M. Ciampolini, N. Nardi and G. P. Speroni, *Coord. Chem. Rev., 1* (1966) 222.
31 W. Wojciechovski, *Inorg. Chim. Acta, 17* (1900) 3194.
32 A. Bencini and D. Gatteschi, *Inorg. Chim. Acta, 31* (1978) 11.
33 J. H. Van Vleck, *The Theory of Electronic and Magnetic Susceptibilities*, Oxford University Press, London, 1933.
34 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev., 5* (1970) 143.
35 I. E. Grey and P. W. Smith, *Aust. J. Chem., 24* (1971) 73.
36 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem., 14* (1975) 1944.