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SPECTRAL AND MAGNETIC STUDIES ON NORMAL COBALT(II) PLANAR AND COBALT(III) OCTAHEDRAL, SPIN-CROSSOVER COBALT(III) OCTAHEDRAL AND PLANAR–TETRAHEDRAL COBALT(II) CARBODITHIOATES

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Abstract—Five cobalt(II) complexes, a normal complex Co(4-PPipzcdt)$_2$ (4-PPipzcdt = 4-phenylpiperazine-1-carbodithioate), and four zwitterionic complexes, Co(4-PPipzcdtH)$_2$X$_2$ and Co(4-MPipzcdtH)$_2$X$_2$ (X = Cl, Br; 4-PPipzcdtH = 4-phenylpiperazine-1-carbodithioic acid, 4-MPipzcdtH = 4-methylpiperazine-1-carbodithioic acid), have been synthesized. Normal cobalt(III) complexes of the type Co(4-MPipzcdt)$_3$ and Co$_2$ {2-MPipz(cdt)$_2$}$_3$ (2-MPipz(cdt)$_2$ = 2-methylpiperazine-1,4-dicarbodithioate) and two zwitterionic cobalt(III) complexes of the type Co(4-MPipzcdtH)$_3$X$_3$ (X = Cl, Br) have also been obtained. In addition to the room temperature IR and electronic spectra and magnetic susceptibility studies, all the complexes, except the normal Co(4-MPipzcdt)$_3$ and Co(4-PPipzcdt)$_2$ and zwitterionic Co(4-MPipzcdtH)$_3$Cl$_3$, have been investigated by variable-temperature magnetic susceptibility measurements. The results of the variable-temperature magnetic susceptibility studies suggest that two cobalt(II) carbodithioates exhibit a square planar–tetrahedral equilibrium, while two cobalt(III) octahedral carbodithioates show a spin-crossover phenomenon.

In their reaction with cobalt(II) salts, the dithiocarbamate ligands in general yield cobalt(III) compounds[1,2] because of (i) larger ligand field stabilization energy in cobalt(III) complexes (a d^6 system) and (ii) the propensity of dithiocarbamate ligands to stabilize relatively higher oxidation states. Though the stability of Co(R$_2$NCS$_2$)$_2$ compounds is known to improve with the use of larger alkyl (R) groups, very few compounds claimed to be cobalt(II) species have been isolated.[3–8] In this paper, in addition to cobalt(III) compounds, a few cobalt(II) compounds with large-size carbodithioate ligands (Fig. 1) are also described: some of these compounds have characteristics hitherto unrecognized for such systems.

EXPERIMENTAL

Synthesis

The ligands 4-methylpiperazine-1-carbodithioic acid, sodium 4-methylpiperazine-1-carbodithioate monohydrate, sodium 4-phenylpiperazine-1-carbodithioate monohydrate and disodium 2-methylpiperazine-1,4-dicarbodithioate dihydrate (Fig. 1) were synthesized by methods described earlier.[9]

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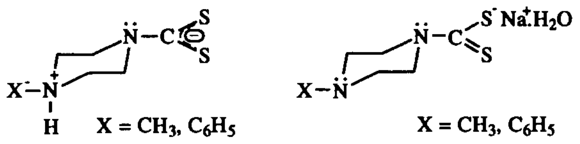
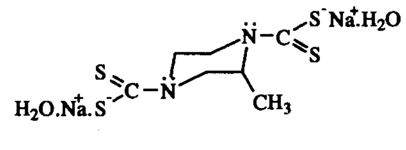


Carbodithioic acid **Sodium carbodithioate monohydrate**



Disodium 2-methylpiperazine-1,4-dicarbodithioate dihydrate

Fig. 1. Structures of the ligands used.

Co(4-MPipzcdt)$_3$. To a saturated methanolic solution of 1.296 g (6.00 mmol) sodium 4-methylpiperazine-1-carbodithioate monohydrate was added with stirring a saturated methanolic solution of cobalt(II) acetate tetrahydrate (0.498 g, 2.00 mmol). A dark green solid separated which was filtered, washed with methanol and air-dried. It was recrystallized from dry chloroform and the crystals were dried *in vacuo* over P_4O_{10}. The proposed structure of the product is shown in Fig. 2a. Found: C, 36.3; H, 5.7; N, 14.0; S, 32.4; Co, 9.9. Calc. for $C_{18}H_{33}N_6S_6Co$: C, 37.0; H, 5.6; N, 14.4; S, 32.9; Co, 10.1%.

Attempted preparation of the compound Co(4-MPipzcdt)$_2$. A green product was obtained by a similar method as for Co(4-MPipzcdt)$_3$, but by mixing aqueous solutions of stoichiometric amounts (1 : 2) of $CoCl_2 \cdot 6H_2O$ and sodium 4-methylpiperazine-1-carbodithioate monohydrate ligand. Found: C, 35.4; H, 5.0; N, 13.1; S, 31.1; Co, 9.9. Calc. for $C_{12}H_{22}N_4S_4Co$: C, 35.2; H, 5.4; N, 13.7; S, 31.3; Co, 14.4%. The procedure for the synthesis of this complex was repeated by using degassed solutions of the starting materials and performing the filtration and drying operations under dry nitrogen. Here, though the percentage for cobalt was found to be 13.4, the percentage for other elements remained the same as mentioned above.

Co(4-PPipzcdt)$_2$ *and* Co$_2${2-MPipz(cdt)$_2$}$_3$. Aqueous solutions of stoichiometric amounts of $CoCl_2 \cdot 6H_2O$ and $Co(OAc)_2 \cdot 4H_2O$ were added with stirring respectively to stoichiometric amounts of an aqueous ethanolic solution of sodium 4-phenylpiperazine-1-carbodithioate prepared *in situ* and an aqueous solution of disodium 2-methylpiperazine-1,4-dicarbodithioate dihydrate. The green product obtained in both cases was filtered *in vacuo*, washed with water, alcohol and diethyl ether, and finally dried *in vacuo* over P_4O_{10}. The structure of Co$_2${2MPipz(cdt)$_2$}$_3$ is shown in Fig. 2b. Found: C, 49.5; H, 4.8; N, 10.5; S, 23.8; Co, 11.0. Calc. for $C_{22}H_{26}N_4S_4Co$ [Co(4-PPipzcdt)$_2$]: C, 49.5; H, 4.9; N, 10.5; S, 24.0; Co, 11.1%. Found: C, 28.9; H, 3.5; N, 9.6; S, 44.0; Co, 13.5. Calc. for $C_{21}H_{30}N_6S_{12}Co_2$ [Co$_2${2-MPipz(cdt)$_2$}$_3$]: C, 29.0; H, 3.5; N, 9.7; S, 44.2; Co, 13.6%.

Co(4-MPipzcdtH)$_2$X$_2$ (X = Cl, Br). The procedure for the preparation of these two green-coloured compounds was the same as that for Fe(4-MPipzcdtH)$_3$ Cl$_3$, as detailed in our paper on iron(III) carbodithioates,[9] except that the stoichiometric ratio of the ethanolic solutions of $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 2H_2O$ with 4-MPipzcdtH was 1 : 2. Structures of the products are shown in Fig. 2c. Found: C, 29.2; H, 4.2; N, 11.6; S, 26.0; Cl, 14.6; Co, 12.4 Calc. for $C_{12}H_{24}S_4Cl_2Co$ [Co(4-MPipzcdtH)$_2$Cl$_2$]: C, 29.9; H, 5.0; N, 11.6; S, 26.5; Cl, 14.7; Co, 12.2%. Found: C, 25.0; H, 4.1; N, 9.9; S, 22.2; Br, 28.0; Co, 10.2. Calc. for $C_{12}H_{24}N_4S_4Br_2Co$ [Co(4-MPipzcdtH)$_2$Br$_2$]: C, 25.2; H, 4.2; N, 9.8; S, 22.4; Br, 28.0; Co, 10.3%.

Co(4-MPipzcdtH)$_3$X$_3$ (X = Cl, Br). For the chloride derivative of the zwitterionic cobalt(III) complex, normal tris(4-methylpiperazine-1-carbodithioato)cobalt(III) complex of undefined quantity was dissolved in dry chloroform and dry HCl gas was passed through this solution. A green solid separated immediately, and was filtered *in*

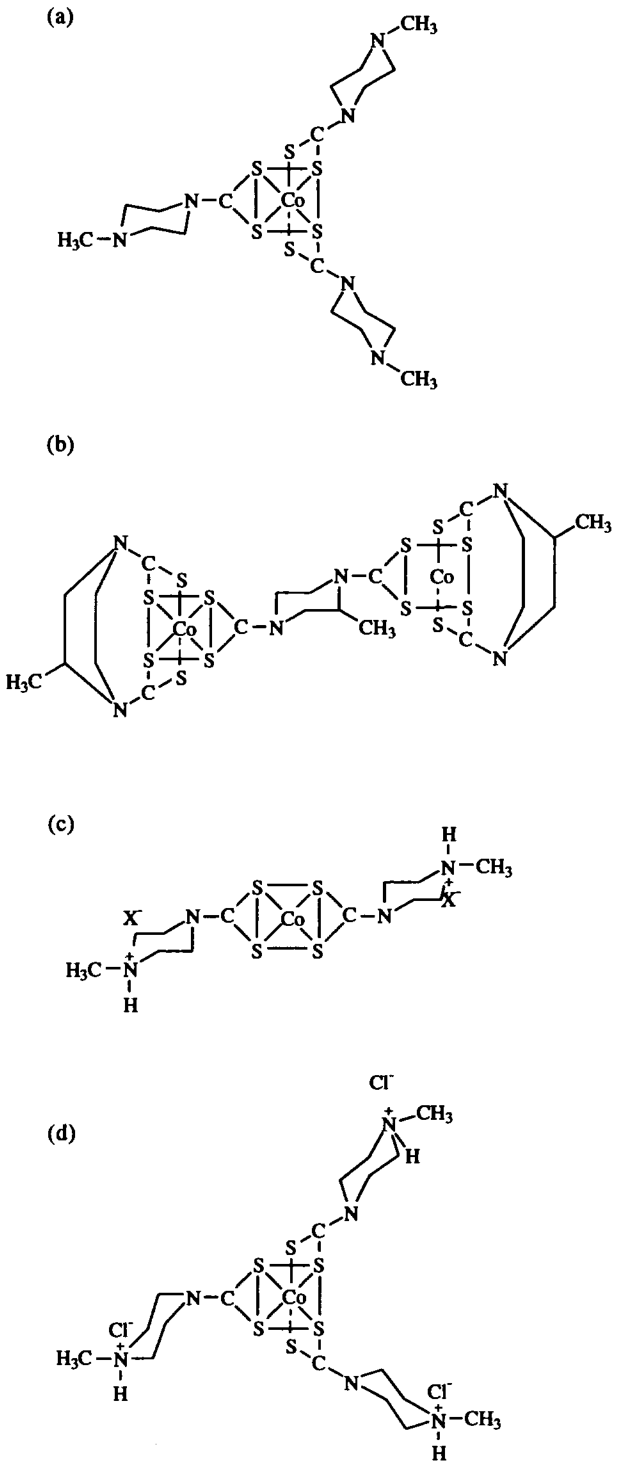


Fig. 2. Proposed structures of some of the cobalt(II) and cobalt(III) carbodithioates.

vacuo, washed with dry chloroform and finally dried *in vacuo* over P_4O_{10}. However, for the bromide derivative, conc. aqueous HBr was added dropwise, with stirring after intervals of 30 min, to the degassed 1:1 dry chloroform–benzene solution of the normal cobalt(III) complex. Addition of the acid was continued until a pale green colour remained in the solution after the precipitate had been allowed to settle. Complete separation of the green product was obtained by adding dry diethyl ether. It was then filtered, washed with dry benzene and dry diethyl ether, and finally air-dried. The structure of Co(4-MPipzcdtH)$_3$Cl$_3$ is shown in Fig. 2d. Found: C, 30.9; H, 5.1; N, 12.0; S, 27.0; Cl, 15.2; Co, 8.1. Calc. for $C_{18}H_{36}N_6S_6Cl_3Co$ [Co(4-MPipzcdtH)$_3$Cl$_3$]: C, 31.1; H, 5.2; N, 12.1; S, 27.7; Cl, 15.3; Co, 8.5%. Found: C, 26.0; H, 4.0; N, 10.0; S, 23.4; Br, 28.5; Co, 7.1. Calc. for $C_{18}H_{36}N_6S_6Br_3Co$ [Co(4-MPipzcdtH)$_3$Br$_3$]: C, 26.1; H, 4.3; N, 10.2; S, 23.2; Br, 29.0; Co, 7.1%.

Co(4-PPipzcdtH)$_2$X$_2$ (X = Cl, Br). Bis(4-phenylpiperazine-l-carbodithioata)cobalt(II) of undefined quantity was dissolved in carefully degassed dry benzene. To this solution conc. aqueous HCl/HBr was added, with stirring, in portions of 1–2 drops after intervals of 10 min. The reaction mixture, kept under nitrogen, was continuously stirred and the addition of the acid was continued until a pale green colour remained in the solution after the precipitate had been allowed to settle. The green precipitate was filtered *in vacuo*, washed several times with degassed dry benzene and finally dried *in vacuo* over P_4O_{10}. Found: C, 43.0; H, 4.3; N, 10.0; S, 21.5; Cl, 12.1; Co, 9.2. Calc. for $C_{22}H_{28}N_4S_4Cl_2Co$ [Co(4-PPipzcdtH)$_2$Cl$_2$]: C, 43.6; H, 4.6; N, 9.2; S, 21.1; Cl, 11.7; Co, 9.7%. Found: C, 37.7; H, 4.0; N, 8.0; S, 18.2; Co, 8.2. Calc. for $C_{22}H_{28}N_4S_4Br_2Co$ [Co(4-PPipzcdtH)$_2$Br$_2$]: C, 38.0; H, 4.0; N, 8.1; S, 18.4; Co, 8.5%.

Elemental analyses and physical measurements

Cobalt in the complexes was determined volumetrically by EDTA titration using Xylenol Orange as an indicator. Chloride and bromide contents in the complexes were determined volumetrically by Volhard's method. Carbon, hydrogen, nitrogen and sulphur analyses and IR and electronic spectral and magnetic susceptibility measurements were made by the methods described earlier.[9]

RESULTS AND DISCUSSION

Cobalt(II) carbodithioates, both normal and zwitterionic, are stable in the solid state for long periods, though it is advisable to store them *in vacuo* or under dry nitrogen. However, they have the tendency to be oxidized in the course of their preparative reaction, i.e. in solution. The Co(4-PPipzcdtH)$_2$X$_2$ (X = Cl, Br) complexes are especially susceptible to aerial oxidation; their synthesis, therefore, had to be done under rigorous oxygen-free conditions. The synthesis of the reported complex Co(4-MPipzcdt)$_2$ was attempted by the method reported in the literature.[4] The preparation of Co(4-MPipzcdt)$_3$ was also attempted by reacting aqueous solutions of $CoCl_2 \cdot 6H_2O$ and sodium carbodithioate in a 1:3 molar ratio. However, the elemental analyses of the two products were found to be similar. The measured room-temperature effective Bohr magneton number, 1.18, for the formula Co(4-MPipzcdt)$_2$ (reported μ_{eff} value is 1.60) suggests that the product is a mixture of cobalt(II) and cobalt(III) species. The attempt to obtain the cobalt(II) complex, Co(4-MPipzcdt)$_2$, by the literature method, even under dry nitrogen, was unsuccessful. However, the reaction of methanolic solutions of $Co(OAc)_2 \cdot 4H_2O$ and sodium 4-methylpiperazine-1-carbodithioate monohydrate in a 1:3 molar ratio yielded a product which analysed as Co(4-MPipzcdt)$_3$ and whose electronic spectral and magnetic susceptibility results (see below) are indicative of a cobalt(III) d^6 ion with a CoS$_6$ core.

IR spectra

The appearance of an additional broad band in the region 3200–3600 cm^{-1}, assignable to ν(N—H), in the IR spectra of complexes having chloride and bromide as counteranions and in free 4-MPipzcdtH, as compared to the normal cobalt and sodium carbodithioates, indicates the existence of 4-MPipzcdt and 1-PPipzcdt ligands as zwitterions in the complexes and in free 4-MPipzcdtH (Table 1). The ν(C$\overset{...}{=}$N) band in normal and zwitterionic carbodithioates of cobalt has been observed at higher energies (1423–1485 cm^{-1}) as compared to the free ligands (1410–1467 cm^{-1}).[10] The positions of the antisymmetric, ν_{as} (SCS), and symmetric, ν_s (SCS), stretching modes of vibrations of the NCS$_2$ group of carbodithioate ligands (at 962–1030 and 903–985 cm^{-1}, respectively) suggest the chelating bidentate mode of the coordination to the metal ion.[11] In the far-IR spectra of some cobalt(II) and cobalt(III) complexes, bands around 355[12] and 360 cm^{-1},[4] respectively, ascribable to M—S stretches, have been observed. However, the simultaneous appearance of two separate metal–sulphur stretching vibrational signals in some other complexes [around 360 and 320 cm^{-1} for cobalt(II), and 355 and 300 cm^{-1} for cobalt(III) carbodithioates] may be considered indicative of the existence of two isomers in such complexes.

Magnetic susceptibility studies

The room-temperature effective Bohr magneton numbers for three cobalt(II) carbodithioates, Co(4-PPipzcdt)$_2$ and Co(4-PPipzcdtH)$_2$X$_2$ (X = Cl and Br), range between 2.41 and 2.44. These μ_{eff} values

Table 1. Partial IR spectral absorptions (cm^{-1}) and probable assignments

Compound	ν(N—H)	ν(C$\overset{...}{=}$N)	ν_{as}(SCS)	ν_s(SCS)	ν(M—S)
4-MPipzcdtH	3600–3200	1442	970	908	—
4-MPipzcdtNa · H_2O	—	1455	990	902	—
4-PPipzcdtNa · H_2O	—	1410	1000	905	—
2-MPipz(cdt)$_2$Na$_2$ · 2H_2O	—	1465	1010	969	—
Co(4-MPipzcdt)$_3$	—	1485	996	913	360
Co$_2${2-MPipz(cdt)$_2$}$_3$	—	1475	1030	985	360, 280
Co(4-PPipzcdt)$_2$	—	1432	989	924	355
Co(4-MPipzcdtH)$_2$Cl$_2$	3600–3240	1476	962	925	360, 320
Co(4-MPipzcdtH)$_2$Br$_2$	3600–3200	1482	966	912	359, 317
Co(4-MPipzcdtH)$_3$Cl$_3$	3640–3160	1473	965	903	360
Co(4-MPipzcdtH)$_3$Br$_3$	3600–3150	1478	962	903	355, 300
Co(4-PPipzcdtH)$_2$Cl$_2$	3640–3160	1423	1004	925	358
Co(4-PPipzcdtH)$_2$Br$_2$	3620–3150	1425	1002	925	355

lie in the range of values corresponding to one unpaired electron for square planar stereochemistry around cobalt(II) d^7 complexes.[13] The magnetic moments for zwitterionic derivatives are not found to vary with temperature between 77 and 299 K. The complexes Co(4-MPipzcdtH)$_2$Cl$_2$ and Co(4-MPipzcdtH)$_2$Br$_2$ exhibit room-temperature magnetic moment values which lie between those expected for tetrahedral ($S = 3/2$) and square planar ($S = 1/2$) cobalt(II) complexes: 4.4 and 2.2, respectively.[14] Also, the magnetic moment values are found to decrease with decrease of temperature (Fig. 3). This may indicate the presence of a square planar–tetrahedral equilibrium. This behaviour is unusual in the sense that no cobalt(II) dithiocarbamate, a d^7 system, is reported to exhibit the above-mentioned phenomenon. To the best of our knowledge, the anomalous magnetic behaviour in

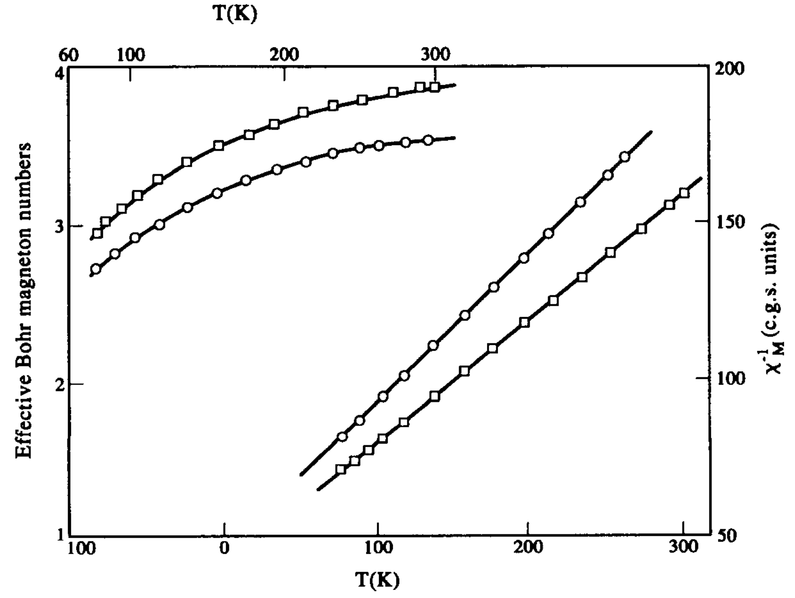


Fig. 3. Variation of molar magnetic susceptibility and effective Bohr magneton numbers of Co(4-MPipzcdtH)$_2$Cl$_2$ (—○—) and Co(4-MPipzcdtH)$_2$Br$_2$ (—□—) with temperature.

the solid state has been ascribed to the planar–tetrahedral thermal equilibrium only once, even in nickel(II) complexes,[15] where it is very common in the solution phase. This anomaly can be attributed to the steric interactions and the crystal packing effects arising from the peculiar structure of the ligand. It is felt that in such rare cases the two stereochemical forms, while retaining their electronic characteristics, are so much removed (distorted) from their ideal forms that a slight required stereochemical rearrangement is made possible by the thermal energy, and is not hampered by the constraints of the solid state. That this is plausible is supported by the evidence that such a rearrangement is indicated to have taken place in the solid state for the stereochemically "rigid" spin-equilibrium system; the observation of changes in various S—Fe—S angles in an extensively studied six-coordinate $Fe(S_2CNR_2)_3$ compound,[16] as the temperature is lowered or the equilibrium is shifted, clearly indicates a decrease, though small, in distortion from octahedral geometry of the FeS_6 core, i.e. movement away from trigonal prismatic towards octahedral geometry. Other possible factors giving rise to anomalous magnetic properties are not considered to be operating here. (i) The magnetic moment values for the dimeric or polymeric structures of $Co^{II}S_4$ leading to octahedral stereochemistry around cobalt(II) (high-spin room temperature $\mu_{eff} \sim 5.1$) with a spin-exchange mechanism operating are not expected to be as low as observed in the present case. This observation is based on the analogy with the well-studied case of $Mn(Et_2dtc)_2$, wherein the observed μ_{eff} values (5.65 at 293 K and 5.15 at 84 K) are attributed to appreciable superexchange antiferromagnetic interactions in the polymerized structure.[17] (ii) The possibility of formation of dithiuram radicals or its complexation with cobalt(I) formed as a result of redox reaction between cobalt(II) and the 4-methylpiperazine-1-carbodithioic acid may also be precluded because generally the dithiocarbamate ligands have a tendency to stabilize cobalt in its +3 oxidation state.

Two cobalt(III) carbodithioates, $Co(4\text{-}MPipzcdt)_3$ and $Co(4\text{-}MPipzcdtH)_3Cl_3$, exhibit the usual diamagnetic behaviour corresponding to low-spin octahedral geometry around the cobalt(III) metal ion.[18] The other two cobalt(III) complexes, $Co_2\{2\text{-}MPipz(cdt)_2\}_3$ and $Co(4\text{-}MPipzcdtH)_3Br_3$, have room-temperature μ_{eff} values (2.50 and 3.45, respectively) lying between zero for low-spin and 5.8 for high-spin octahedral cobalt(III) complexes. The μ_{eff} values are found to decrease with decreasing temperature (Fig. 4). A plausible explanation of this anomalous behaviour is the observance of a spin-crossover phenomenon involving the ${}^1A_{1g}$ and ${}^5T_{2g}$ states. Such behaviour has been recently

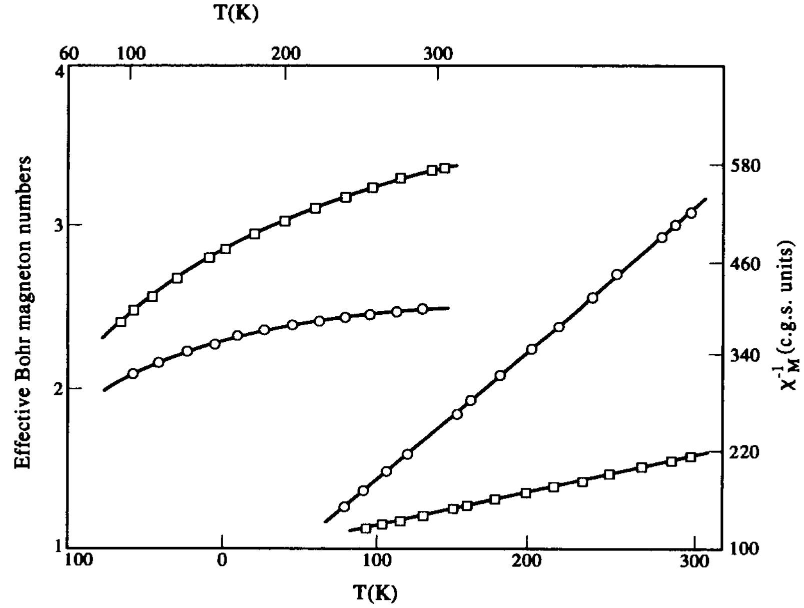


Fig. 4. Variation of molar magnetic susceptibility and effective Bohr magneton numbers of $Co_2\{2\text{-}MPipz(cdt)_2\}_3$ (—○—) and $Co(4\text{-}MPipzcdtH)_3Br_3$ (—□—) with temperature.

reported for cobalt(III) complexes with oxygen tripod ligands.[19] The stoichiometry of the Co^{III}S$_6$ complexes overrules the possibility of antiferromagnetism being a factor in reducing the magnetic moment: Co(4-MPipzcdtH)$_3$Br$_3$ cannot have a polymeric structure and Co$_2${2-MPipz(cdt)$_2$}$_3$, despite presumably having a dinuclear structure (Fig. 2), cannot have superexchange interactions since the link between two cobalt(III) atoms is prevented by a large saturated group.

Electronic spectra

In the electronic diffuse reflectance spectra of three cobalt(II) complexes, Co(4-PPipzcdt)$_2$ and Co(4-PPipzcdtH)$_2$X$_2$ (X = Cl and Br), the four observed absorption bands are indicative of D_{2h} symmetry for the cobalt(II) d_7 planar stereochemistry.[20] A well-defined strong band occurring at 14,300–15,400 cm^{-1} is assigned to the transitions $^2B_{1g} \leftarrow {}^2A_g$ ($d_{x^2-y^2} \rightarrow d_{xy}$) and $^2B_{3g} \leftarrow {}^2A_g$ ($d_{xz} \rightarrow d_{xy}$). A shoulder around 18,000–20,000 cm^{-1} and another strong band at 25,000 cm^{-1} are assigned to the $^2B_{2u} \leftarrow {}^2A_g$ ($d_{xz} \rightarrow$ L (π^*)) and $^2B_{3u} \leftarrow {}^2A_g$ ($d_{yz} \rightarrow$ L (π^*)) metal-to-ligand charge transfer transitions, respectively. In addition to the bands that appear in the d^8 system, a low-energy *d–d* band appears around 5800–6300 cm^{-1} for the cobalt(II) d^7 carbodithioates under study and this has been attributed to the transitions $^2B_{3g} \leftarrow {}^2A_g$ ($d_{yz} \rightarrow d_{x^2-y^2}$) and $^2B_{2g} \leftarrow {}^2A_g$ ($2b_{2g} \rightarrow 4a_g$, $d_{xz} \rightarrow d_{x^2-y^2}$).

Cobalt(II) carbodithioates Co(4-MPipzcdtH)$_2$X$_2$ (X = Cl and Br) exhibit four absorption bands in their electronic diffuse reflectance spectra, in the regions ~24,000, 19,000–19,610, 14,815 and 5260–7150 cm^{-1}. In general, cobalt(II) in tetrahedral stereochemistry[14] exhibits only two absorption bands around 4000–8000 and 13,000–16,500 cm^{-1}, and in square planar geometry[20] complexes absorb in the regions ~8500, 14,000–15,000, 20,000 and 25,000 cm^{-1}. Thus, the electronic spectra of the two cobalt(II) carbodithioates under study are compatible with the magnetic conclusions.

In the electronic diffuse reflectance spectra of the two cobalt(III) carbodithioates Co(4-MPipzcdt)$_3$ and Co(4-MPipzcdtH)$_3$Cl$_3$, the three observed bands at 15,385, 20,000 and 23,530 cm^{-1} are assigned to the octahedral geometry of low-spin cobalt(III) complexes. The splitting of the lower energy band, ascribable to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition in O_h symmetry into two components appearing at 15,385 and 20,000 cm^{-1}, suggests that the complexes have tetragonally distorted structures. The observed absorption bands for these complexes are therefore assigned to the transitions $^1E_g \leftarrow {}^1A_{1g}$, $^1A_{2g} \leftarrow {}^1A_{1g}$ and $^1B_{2g}$, $^1E_g \leftarrow {}^1A_{1g}$, respectively, in D_{4h} symmetry.[13]

The cobalt(III) carbodithioates Co$_2${2-MPipz(cdt)$_2$}$_3$ and Co(4-MPipzcdtH)$_3$Br$_3$, which show anomalous magnetic behaviour, exhibit two intense bands falling in the regions 20,000–21,000 and 14,300–15,400 cm^{-1}, and a weak band in the range 8300–10,000 cm^{-1}, in their electronic diffuse reflectance spectra. The two high-energy bands of high intensity may be assigned to the spin-allowed $^1T_{2g} \leftarrow {}^1A_{1g}$ and $^1T_{1g} \leftarrow {}^1A_{1g}$ transitions and the third weak band to the spin-forbidden $^3T_{2g}$, $^3T_{1g} \leftarrow {}^1A_{1g}$ transitions of low-spin octahedral cobalt(III) complexes. In view of the conclusions of the magnetic susceptibility studies, the middle-energy band (14,300–15,400 cm^{-1}), which is quite a strong band, may also contain an absorption due to the $^5E_g \leftarrow {}^5T_{2g}$ transition. The unsymmetrical shape of this band supports the contention of this band resulting from the overlap of absorptions due to the $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^5E_g \leftarrow {}^5T_{2g}$ electronic transitions.

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