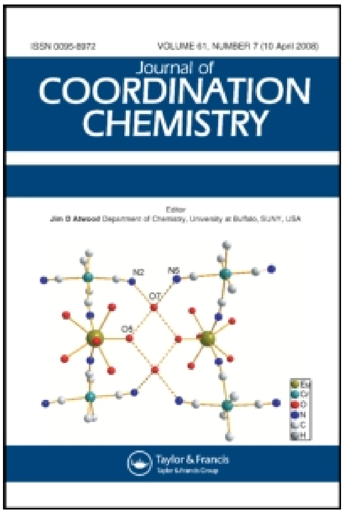

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF DITHIOCARBAMATO COMPLEXES OF SOME 3d-METAL IONS

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF DITHIOCARBAMATO COMPLEXES OF SOME 3d-METAL IONS

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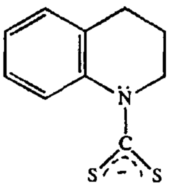
Various aspects of the coordination chemistry of Cr(III), Mn(III), Fe(III), Co(II) and Cu(II) with tetrahydroquinoline and tetrahydroisoquinoline dithiocarbamates have been investigated. Under appropriate conditions, both the ligands form solid complexes of composition $M(dtc)_3$ [M = Cr(III), Mn(III) and Fe(III)] and $M(dtc)_2$ [M = Co(II) and Cu(II)]. The complexes have been characterized by analyses, infrared, electronic and EPR spectroscopy and magnetic susceptibility studies. Infrared spectra indicate the ligands to be isobidentate. Electronic spectra are characteristic of an MS_6 chromophore with a distorted octahedral structure for Cr(III), Mn(III) and Fe(III) and of an MS_4 chromophore with a square planar structure for Co(II) and Cu(II).

KEYWORDS: dithiocarbamates, first-row complexes, esr, electronic structure

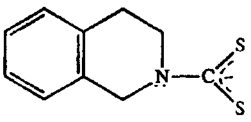
INTRODUCTION

Metallic dithiocarbamates have received much interest because of their diverse applications in such fields as vulcanisation, high pressure lubrication and as fungicides and pesticides.[1,2] Dithiocarbamato complexes of bivalent and tervalent transition metal ions have interesting electronic and magnetic properties. Tris(dithiocarbamato) iron(III) complexes are known to be classical spin crossover systems.

Although much work has been carried out on mono and disubstituted dithiocarbamates, very few heterocyclic dithiocarbamates have been studied. In continuation of our studies of heterocyclic dithiocarbamato ligands we report the synthesis and characterization of complexes of chromium(III), manganese(III), iron(III), cobalt(II) and copper(II) with tetrahydroquinoline and tetrahydroisoquinoline dithiocarbamates **I**, Nathq-dtc and **II**, Nathiq-dtc.



I



II

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Material and Methods

Tetrahydroquinoline (thq) and tetrahydroisoquinoline (thiq) were purchased from Aldrich. Both ligands were prepared as reported elsewhere.[3] Metal sulphates and other reagents were of high purity and were used as obtained without further purification.

SYNTHESIS OF COMPLEXES

In a typical preparation of the complexes, 2.5 mmol of the corresponding metal sulphate [(Cr(III), Mn(III), Fe(III)] dissolved in 25 cm^3 of ice cold water was added drop-wise to 7.5 mmol of the corresponding dithiocarbamate. For Co(II) and Cu(II) complexes, 2.5 mmol of metal sulphate in 25 cm^3 of ice cold water was added to 5.0 mmol of ligand. The reaction mixture was stirred for 1 h and then filtered. The resulting coloured complex was washed with an excess of deionized water and vacuum dried Samples of high purity were obtained directly. Purity was also checked by tlc. Repreated syntheses and elemental analyses gave reproducible results. C,H,N and metal analyes gave satisfactory results for the given stoichiometries.

Physical measurements

Conductivity measurements were carried out with a Beckman Re-18A conductivity bridge using freshly prepared 10^{-3}M solutions in DMF at 300±0.1°K. Room temperature magnetic susceptibility measurements were made by the Guoy method using $Hg[Co(NCs)_4]$ as calibrant. Infrared spectra (KBr and Csl discs) were recorded on Perkin-Elmer and Shimadzu IR spectrophotometers in the 4000–200 cm^{-1} range. Electronic spectra were recorded on a Beckman DU64 spectrophotometer in the 200–900 nm range. X-Band EPR spectra were recorded on a JEOL JES-3XG ESR spectrometer with a variable temperature liquid nitrogen cryostat.

RESULTS AND DISCUSSION

All the complexes are coloured, microcrystalline powders. They are stable under ambient conditions, insoluble in water and most organic solvents except for $CHCl_3$, CH_2Cl_2, DMF and DMSO. Conductivity measurements in DMF showed that the complexes are non-electrolytes. Complexes of Cr(III), Mn(III) and Fe(III) had the formula $M(dtc)_3$ whereas Co(II) and Cu(II) conformed to the $M(dtc)_2$ type.

IR spectra

Three regions in the IR spectra of the $M(R_2dtc)_n$ complexes are of interest. The 1450–1550 cm^{-1} region is associated primarily with the 'thioureide' vibration and is attributed to the $C=N$ vibration of the $S_2C\text{-}NR_2$ bond. An increase in the double bond character of the C-N results in higher frequencies for this vibration.[2] A second region between 950–1050 cm^{-1} is associated with the ν(CSS) vibration and has been used effectively in differentiation between monodentate and bidentate R_2dtc ligands.[4] Finally, the 300–400 cm^{-1} region is associated with M-S vibrations.

A persual of data in Table 1 reveals that the C-N stretching frequency upon complexation increases compared with the Na salts of both ligands but the increase is greater for thiq-dtc. Thus the double bond character in the case of thiq-dtc and its complexes is higher than in the thq-dtc and its complexes. In all complexes, a single sharp band present in the 970–990 cm^{-1} range has been attributed to asymmetric v(CSS). This is further confirmed by the analysis of the position of v(C-N) which undergoes a blue shift upon complexation for both the ligands. In the far IR, two additional bands are observed. One in the 385–395 cm^{-1} region has been assigned to v(M-S), whereas the other at 240–250 cm^{-1} could be attributed to normal modes involving both M-S and ring vibration modes.

Magnetic moments and electronic spectra

The electronic spectra of all complexes were recorded in chloroform and band positions with tentative assignments are given in Table 2.

Cr(III) complexes

The complexes show magnetic moments in the range 3.82–3.96 B.M. consistent with other octahedral Cr(III) species reported earlier.[5–7] Three strong absorption bands are present in the visible region. The position and intensity of the bands are consistent with those reported for other complexes containing a CrS_6 chromophore with a distorted octahedral structure.[7–9]

Mn(III) Complexes

Magnetic moments for both Mn(III) compounds lie in the range 4.80–4.84 B.M. revealing the high spin nature of the complexes.[10,11] Electronic spectra show a strong band at *ca* 20000 cm^{-1} with a shoulder at 18000 cm^{-1}. The intense band seems to be due to ligand to metal charge transfer; the shoulder may be assigned to the $^5T_{2g} \leftarrow {}^5E_g$ transition.

Table 1 Significant infrared bands of the complexes.

Compound	νC–N	νC–S	νM–S	δM–S & ring vibrations
Na(thq-dtc).2H_2O	1450	980		
Cr(thq-dtc)$_3$	1456	990	390	245
Mn(thq-dtc)$_3$	1458	985	395	250
Fe(thq)-dtc)$_3$	1458	985	395	250
Co(thq-dtc)$_2$	1460	980	385	245
Cu(thq-dtc)$_2$	1465	985	390	250
Na(thiq-dtc).2H_2O	1465	975		
Cr(thiq-dtc)$_3$	1476	980	390	245
Mn(thiq-dtc)$_3$	1480	982	395	248
Fe(thiq-dtc)$_3$	1475	990	390	242
Co(thiq-dtc)$_2$	1480	985	385	245
Cu(thiq-dtc)$_2$	1485	988	388	250

Table 2 Magnetic moments and electronic spectroscopic data for the complexes.

Complex	μeff(B.M.)	Band position (log ε)	Assignment	Comment
Cr(thq-dtc)$_3$	3.96	16129(2.40)	$^4T_{2g} \leftarrow {}^4A_{2g}$	10 Dq = 16,129
		18812(2.64)	$^4T_{1g}(F) \leftarrow {}^4A_{2g}$	Distorted O$_h$
		20000(3.70)	$e_g \leftarrow \pi$(C.T.)	around Cr(lll)
		21867(3.75)	$\pi^* \leftarrow n$(I.L.T.)	
		32467(2.89)	$^4T_{1g}(P) \leftarrow {}^4A_{2g}$	
		35211(4.76)		
		41666(5.33)	$\pi^* \leftarrow \pi$(I.L.T.)	
Cr(thiq-dtc)$_3$	3.82	16234(2.41)	$^4T_{2g} \leftarrow {}^4A_{2g}$	10 Dq = 16,234
		19106(2.64)	$^4T_{1g}(F) \leftarrow {}^4A_{2g}$	Distorted O$_h$
		20000(3.70)	$e_g \leftarrow \pi$(C.T.)	around Cr(lll)
		21367(3.75)	$\pi^* \leftarrow n$(I.L.T.)	
		31847(2.88)	$^4T_{1g}(P) \leftarrow {}^4A_{2g}$	
		38461(4.76)		
		41666(5.33)	$\pi^* \leftarrow \pi$(I.L.T.)	
Mn(thq-dtc)$_3$	4.80	18382(2.45)	$^5T_{2g} \leftarrow {}^5E_g$	Highly distorted
		20000(3.70)	$e_g \leftarrow \pi$(C.T.)	O$_h$ around
		21367(3.75)	$\pi^* \leftarrow n$(I.L.T.)	Mn(lll)
		32697(4.76)		
		41666(5.33)	$\pi^* \leftarrow \pi$(I.L.T.)	
Mn(thiq-dtc)$_3$	4.84	17730(2.46)	$^5T_{2g} \leftarrow {}^5E_g$	as above
		20000(3.70)	$e_g \leftarrow \pi$(C.T.)	
		21637(3.75)	$\pi^* \leftarrow n$(I.L.T.)	
		32697(4.76)		
		41666(5.22)	$\pi^* \leftarrow \pi$(I.L.T.)	
Fe(thq-dtc)$_3$	3.40	16200(2.30)	$d \leftarrow d$	Characteristic
		19100(2.42)	$d \leftarrow d$	six-coordinate
		20000(3.70)	$e_g \leftarrow \pi$(C.T.)	octahedral
		21367(3.75)	$\pi^* \leftarrow n$(I.L.T.)	mixture
		27482(2.85)	$d \leftarrow d$	
		35461(4.76)		
		41666(5.33)	$\pi^* \leftarrow \pi$(I.L.T.)	
Fe(thiq-dtc)$_3$	3.42	16360(2.31)	$d \leftarrow d$	as above
		19242(2.42)	$d \leftarrow d$	
		20000(3.70)	$e_g \leftarrow \pi$(C.T.)	
		21367(3.75)	$\pi^* \leftarrow n$(I.L.T.)	
		26881(2.85)	$d \leftarrow d$	
		33784(4.70)		
		38461(4.76)	$\pi^* \leftarrow \pi$(I.L.T.)	
		41666(5.35)		
Co(thq-dtc)$_2$	2.30	15291(2.58)	$^2B_{1g}$, $^2B_{2g} \leftarrow {}^2A_g$	Characteristic
		23255(3.65)		low spin square
		26315(3.80)	$e_g \leftarrow \pi$(C.T.)	planar Co(II)
		39063(4.76)		
		41666(5.33)	$\pi^* \leftarrow \pi$(I.L.T.)	
Co(thiq-dtc)$_2$	2.34	15291(2.60)	$^2B_{1g}$, $^2B_{2g} \leftarrow {}^2A_g$	as above
		23255(3.66)		
		26315(3.80)	$e_g \leftarrow \pi$(C.T.)	
		33783(4.76)		
		41666(5.33)	$\pi^* \leftarrow \pi$(I.L.T.)	
Cu(thq-dtc)$_2$	1.81	22727(2.69)	$^2E_g \leftarrow {}^2B_{1g}$	Square planar
		31747(3.80)	$e_g \leftarrow \pi$(C.T.)	Cu(ll)
		38461(4.76)		
		41666(5.32)	$\pi^* \leftarrow \pi$(I.L.T.)	
Cu(thiq-dtc)$_2$	1.84	22522(2.70)	$^2E_{1g} \leftarrow {}^2B_{1g}$	as above
		32895(3.80)	$e_g \leftarrow \pi$(C.T.)	
		38461(4.76)		
		41660(5.33)	$\pi^* \leftarrow \pi$(I.L.T.)	

C.T. = Charge transfer: I.L.T. = Intra ligand transfer.

Fe(III) Complexes

Magnetic moments are 3.40 and 3.42 B.M., intermediate between the spinfree and spin-paired configuration as suggested by Figgis and Lewis.[12] Polynuclear complexes are also found to exhibit similar abnormal magnetic moments values. Mitchell and Parker[13] have suggested that the most plausible explanation of such magnetic properties is the presence of iron(III) in spin state $S = 3/2$, because the low magnetic moment cannot be explained by interaction between iron atoms and must be due to a change of spin state. The most plausible spin state in such a case is $S = 3/2$ (spin only moment 3.87 B.M.). This is evidenced by complicated electronic spectra and EPR features (*vide infra*).

The electronic spectra of the complexes display some eight well-defined absorptions bands. However, unequivocal assignment may not be possible due to the spin equilibrium. Electronic spectra at room temperature consist of a mixture from both high and low spin species and $^6A_1$ and $^2T_2$ populations vary with modification of ligand and with pressure and temperature.

Co(II) Complexes

The Co(II) complexes have magnetic moments from 2.30–2.34 B.M. and indicate square planara geometry.[16] A well defined band at 15291 cm^{-1} is assigned to $^2A_{1g} \rightarrow {}^2B_{1g}$ and $^2A_g \rightarrow {}^2B_{2g}$.[17] Simple EPR spectra also suggest a low spin tetracoordinate planar structure.[18] Since Co(II) is highly susceptible to aerial oxidation, especially in the presence of sulphur donors, very few definite studies on electronic spectra have been reported. In fact, very few stable complexes with a CoS_4 chromophore are known and only with bulkier systems than in the present case.[19]

Cu(II) Complexes

Magnetic moments of the Cu(II) complexes at room temperature lie in the range 1.81–1.84 B.M., as expected for a d^9 system. Electronic spectra show a low intensity band around 22500 cm^{-1} ($^2E_g \leftarrow {}^2B_{1g}$) and are consistent with square planar Cu(II) with D_{2h} symmetry.[20–22]

EPR studies

X-Band EPR spectra of powdered samples of the complexes were recorded at liquid nitrogen temperature; bonding parameters are presented in Table 3.

Cr(III) Complexes

EPR spectra of Cr(thq-dtc)$_3$ and Cr(thiq-dtc)$_3$ give one broad signal, which is practically isotropic. This may be attributed to the main $-1/2 \rightarrow +1/2$ transition. It is clear that ZFS in these complexes is large since only one signal has been observed. In the CFT, g is given by

$$g = 2.0023\text{-}8\ \lambda/\Delta(T_{2g})$$

where λ is the effective spin orbit coupling constant. Owen[23] noted that reduction of the spin orbit coupling constant from the free ion value of 90 cm^{-1} for Cr(III) can

Table 3 EPR parameters for the metal dithiocarbamates.

Compound	Temp. (K)	$g_{\parallel}$	$g_{\perp}$	<g>	$A_{\parallel} \times 10^{-4}$	$A_{\perp} \times 10^{-4}$	<A> $\times 10^{-4}$	λ	γ	G
Cr(thq-dtc)$_3$	173			1.987				30.8	0.34	
Cr(thiq-dtc)$_3$	173			1.982				41.2	0.46	
Mn(thq-dtc)$_3$	143			1.960						
Mn(thiq-dtc)$_3$	143			1.982						
Fe(thq-dtc)$_3$	143			2.109 4.102						
Fe(thiq-dtc)$_3$	143			2.118 4.104						
Co(thq-dtc)$_2$	173	1.990	2.005	1.902	25.00	1.78	9.52			
Co(thiq-dtc)$_2$	173	1.990	2.001	1.997	28.57	1.79	10.72			
Cu(thq-dtc)$_2$	143	2.052	2.016	2.029	25.00	7.67	13.45			2.89
Cu(thiq-dtc)$_2$	143	2.062	2.028	2.028	18.33	10.00	12.78			2.21

be taken as a measure of metal ligand covalency. It is possible to define a covalency parameter, γ, as the ratio of spin orbit coupling constant for the complex and for the free Cr(III) ion ($\gamma = \lambda/90\,\mathrm{cm}^{-1}$). The complexes exhibit values lower than related dithiocarbamato complexes,[24] indicating a greater degree of σ-covalency in the present case.

Mn(III) complexes

One intense absorption was observed in EPR spectra. As with earlier reports on Mn(III) dithiocarbamates,[25,26] the <g> values of the present systems are comparable. Hence it appears that the signal might arise from an electron at or near the sulphur atom. It might be due to tetragonally distorted octahedral structures making ψ1, the ground state as for Mn(III) in TiO_2.[27]

Fe(III) Complexes

There are few reports of EPR spectra of Fe(III) dithiocarbamates, mainly because high spin Fe(III) spectra are difficult to interpret and low spin Fe(III) spectra are difficult to observe, except at very low temperature. In the presence case, both systems were EPR silent at RT but two signals were observed at low temperature (143°K). This indicates that Fe(thq-dtc)$_3$ and fe(thiq-dtc)$_3$ are potential spin crossover systems with spin equilibrium between $S = 5/2$ and $S = 1/2$ states ($^6A_{1g} \Leftrightarrow {}^2T_{2g}$) EPR spectra of Fe(thq-dtc)$_3$ and Fe(thiq-dtc)$_3$ are structurally similar except for their g values. The spectra show a broad and intense signal at g 2.109 and 2.118 and a very weak signal at g 4.102 and 4.104. Taking the magnetic moment at RT into consideration, neither of the two spin states could be the origin of the signal; hence a mixed spin state may be proposed.

In spite of the difficulty previous workers had in obtaining Fe(dtc)$_3$ EPR signals, Flick and Gelerintor[28] presented evidence for the existence of spin equilibrium in Fe(dch-dtc)$_3$ by identifying paramagnetic lines assocated with both spin states. The observation is in line with the present system except for the fact that they observed an additional signal at $g \approx 6.5$.

The EPR characteristic of a high spin d^5 system have been discussed in many papers.[29,30] The spectra can be interpreted in terms of the following Hamiltonian

$$H = g\beta HS + D[S_z^2 - 1/3\ S(S + 1)] + E[S_x^2 - S_y^2]$$

where all the symbols have their usual significance. The nature of the spectra observed are highly dependent on the terms D and E. If D and E are zero, the anisotropic absorption line with a g value slightly greater than 2 is observed. If D and E are finite but small (0.001–0.1 cm^{-1}), five transitions are observed.[31] The low field signal at $g \approx 4.1$ in the present complexes is typical for $D = O$, $E \neq O$ and E is greater than $g\beta H$.

Co(II) Complexes

To our surprise, no report regarding $^{59}Co(II)$ dithiocarbamates has been found in spite of oxidation state controversy. EPR spectra of Co(II) complexes with both ligands give rise to identifiable lines from $^{59}Co(I = 7/2)$ hyperfine splitting. A well defined hyperfine structure was observed in the parallel region but the perpendicular is unresolved. Observation of hyperfine splitting suggests that both the systems form a magnetically dilute lattice.

Cu(II) Complexes

EPR spectra of both the Cu(II) complexes are identical in appearance with an intense signal at high field and a weak signal at low filed and this reflects an axially symmetric environment. The g values are nearly the same for both the complexes and indicate sulphur coordination; $g_{\parallel}$ values being less than 2.3 are an indication of significant covalent bonding in the complexes.[32] The trend $g_{\parallel} > g_{\perp} > 2.0023$, observed for both the complexes is consistent with a $d_{x^2-y^2}$ ($^2B_{1g}$) ground state. In axial symmetry **G** is a measure of the exchange interaction between Cu(II) centres in a polycrystalline solid.[33] If **G** > 4, exchange interaction is negligible, while **G** < 4 indicates considerable exchange interaction in solid complexes.[34] Following this criterion, considerable crystal lattice interactions are present.

CONCLUSIONS

Both ligands behave as isobidentates as evidenced by infrared spectra. $Fe(dtc)_3$ complexes prove to be potential spin crossover systems. Co(II) is stabilised in its + 2 oxidation state due to the bulkier nature of the ligands. EPR spectra and conductance studies prove that M-L bonds are significantly covalent. Observation of Co(II) hyperfine splitting suggests that both the complexes form a magnetically dilute lattice. Both ligands, with Cr(III), Mn(III) and Fe(III), form complexes with distorted octahedral structures whereas with Co(II) and Cu(II) they form complexes with square planar geometry.

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