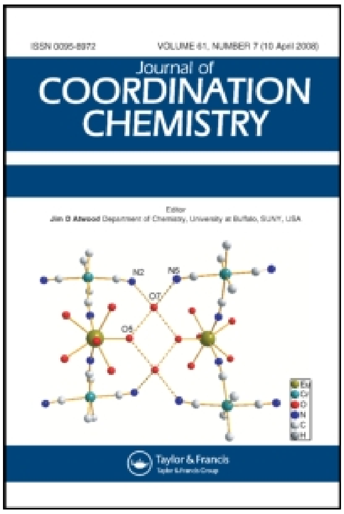

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THE CO-ORDINATION CHEMISTRY OF DIVALENT COBALT, NICKEL AND COPPER Part III. Five-coordinate Cobalt(II) Complexes with Bis(Acetamido)thioether derivatives

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THE CO-ORDINATION CHEMISTRY OF DIVALENT COBALT, NICKEL AND COPPER

Part III. Five-coordinate Cobalt(II) Complexes with Bis(Acetamido)thioether derivatives

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Preparation and properties of new cobalt(II) complexes using ligands with OSO sets of donor atoms, viz. bis(N,N-dimethylacetamido)-thioether (TTDA) and bis(N-methyl-N-phenylacetamido)thioether (DTDA), are reported. Magnetic, spectral and non-aqueous conductivity data were obtained. Penta-coordinate structures are proposed for solid $CoX_2 \cdot TTDA$ ($X = Cl^-, Br^-, I^-, NO_3^-$ and NCS^-) and $CoX_2 \cdot DTDA$ ($X = Cl^-$, Br^- and NCS^-). Similar data for $Co(NO_3)_2 \cdot DTDA$ and $Co(ClO_4)_2 \cdot 2TTDA$ strongly suggest distorted octahedral structures for these. Gaussian analysis on the solid reflectance spectra were done.

INTRODUCTION

In parts I[1] and II[2] of this series penta-coordinate copper(II) complexes of the first neutral tridentate ligands having OSO sets of donor atoms, viz. bis(N,N-dimethylacetamido)thioether (TTDA) and bis(N-methyl-N- phenylacetamido)thioether (DTDA), were reported. An X-ray crystal structure determination of one of these,[3] i.e. $CuCl_2 \cdot TTDA$, indicated a distorted square pyramidal structure in which one copper to amide oxygen (the apicle atom) is 0·25Å longer than the other copper to amide oxygen bond. Corresponding splits of about $30\,cm^{-1}$ in the ligand carbonyl stretch frequency bands in the infrared spectrum were also obtained in the chloro and bromo complexes. During a preliminary investigation no such splittings were obtained for the corresponding cobalt(II) compounds. In the light of these possible structural differences and since these ligands are the first neutral tridentate ligands having OSO sets of donor atoms it was of interest to isolate a number of similar cobalt(II) compounds especially with the purpose of studying their structure, electronic spectral and magnetic properties. The following compounds were, therefore, prepared; $CoX_2 \cdot TTDA$ (where $X = Cl^-, Br^-, I^-, NCS^-$ and NO_3^-), and $CoX_2 \cdot 2TTDA$ (where $X = Cl^-, NCS^-$ and NO_3^-) and $CoX_2 \cdot 2TTDA$ (where $X = I^-$ and ClO_4^-). All of these proved to be spin-free complexes. Penta-coordinate structures are proposed for all except the latter two and $Co(NO_3)_2 \cdot DTDA$ which are assumed to be distorted octahedral.

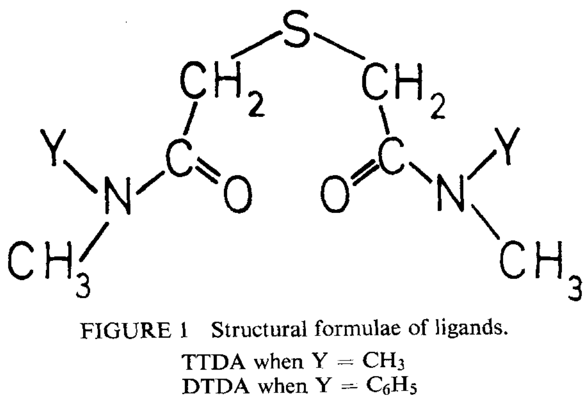

FIGURE 1 Structural formulae of ligands.
TTDA when $Y = CH_3$
DTDA when $Y = C_6H_5$

EXPERIMENTAL

Bis(N,N-dimethylacetamido)thioether (TTDA) and bis(N-methyl-N-phenylacetamido)thioether (DTDA) were prepared as previously reported.[1]

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Preparation of Complexes

All the complexes were washed with ethyl acetate (twice) and finally three times with either ether or petroleum ether and dried in vacuo unless stated otherwise.

(i) *Chloro and bromo complexes* A concentrated methyl cyanide solution of the ligand, in slight excess, was added to a concentrated methyl cyanide solution of the anhydrous cobalt salt. From this mixture

(a) blue slightly hygroscopic crystals of $CoBr_2 \cdot TTDA$ formed upon standing,
(b) a light blue slightly hygroscopic solid $CoCl_2 \cdot TTDA$ was precipitated upon addition of a 5 : 1 mixture of methylene chloride and ethyl acetate, and
(c) light blue slightly hygroscopic $CoCl_2 \cdot DTDA$ was precipitated upon addition of ether.

(ii) *Thiocyanato complexes* Equivalent amounts of anhydrous cobalt chloride and potassium thiocyanate were each dissolved in the minimum of boiling absolute alcohol and then mixed. The resulting potassium chloride precipitate was filtered off. To 20 ml. of the dark blue filtrate, containing 7.7 m.mole of $Co(NCS)_2$, was added ligand (7.8 m.mole) in absolute alcohol (5 ml.). Bright blue non-hygroscopic $Co(CNS)_2 \cdot TTDA$ and $Co(CNS)_2 \cdot DTDA$ crystallized out upon standing.

(iii) *Nitrato complexes* To a methyl cyanide solution (15 ml) of $Co(NO_3)_2 \cdot 6H_2O$ (3.4 m.mole) was added 2,2-dimethoxypropane (10 ml.) and left to stand for 3 hours. A concentrated methyl cyanide solution (5 ml.) of the ligand (3.5 m.mole DTDA or 9.8 m.mole TTDA) was then added. The solution turned mauve. A mauve solid was precipitated by addition of ether and treated as follows:

(a) DTDA complex. This was now vacuum dried. The non-hygroscopic solid product was analysed.
(b) TTDA complex. The mauve solid was redissolved in hot methyl cyanide, a further 2 m.mole ligand was added whereupon the solution turned blue. A very hygroscopic blue $Co(NO_3)_2 \cdot TTDA$ was precipitated by ethyl acetate, vacuum dried and analysed.

(iv) *Iodo complexes* To a green n-butanol solution (25 ml.) of anhydrous cobalt iodide (2.25 m.mole) was added a solution of the ligand (2.3 m.mole) in the same solvent (5 ml.). A green solid precipitated immediately. This was vacuum dried at 80° C for four hours when buff hygroscopic $CoI_2 \cdot TTDA$ was obtained.

When five times excess of TTDA was used in the above procedure brownish red crystals of $CoI_2 \cdot 2TTDA$ formed.

(v) *Perchlorate complex* To a methyl cyanide solution (25 ml.) of $Co(ClO_4)_2 \cdot 6H_2O$ (3.9 m.mole) was added TTDA (7.9 m.mole) in the same solvent (5 ml.). Pale pink non-hygroscopic $Co(ClO_4)_2 \cdot 2TTDA$ was precipitated by ether from the above solution.

Analytical and Physical Measurements

All analytical and physical measurements were carried out as described previously.[1,2]

RESULTS AND DISCUSSION

Analytical and some physical data of the complexes are given in Table I. The conductivities of the

TABLE I

Analytical and physical data of complexes

Compound	Colour	M.p.[a] °C	%C Calc.	%C found	%H Calc.	%H found	%N Calc.	%N found	%Metal Calc.	%Metal found
$CoCl_2 \cdot TTDA$	Pale blue	224	28.83	27.3	4.79	4.9	8.39	8.3	17.64	17.8
$CoBr_2 \cdot TTDA$	Blue	270d	22.80	22.4	3.78	4.0	6.62	6.5	13.93	13.7
$CoI_2 \cdot TTDA$	Green	293d	18.58	18.2	3.10	3.3	5.42	5.4	11.40	11.4
$Co(NCS)_2 \cdot TTDA$	Bright blue	300d	31.67	31.3	4.22	4.0	14.80	14.6	15.55	15.3
$Co(NO_3)_2 \cdot TTDA$	Dark blue	247d	24.52	24.8	4.09	4.2	14.47	14.2	15.20	15.0
$Co(ClO_4)_2 \cdot 2TTDA$	Pale pink	210d	28.83	28.7	4.81	4.7	8.41	8.2	8.85	9.0
$CoCl_2 \cdot DTDA$	Pale blue	100	47.17	46.6	4.37	4.4	6.11	5.9	12.87	12.6
$Co(NCS)_2.DTDA$	Bright blue	150	47.72	47.2	3.98	4.1	11.13	10.7	11.72	11.8
$Co(NO_3)_2 \cdot DTDA$	Dark mauve	99	42.28	41.6	3.91	4.1	10.96	10.6	11.53	11.7

[a] d-decomposes

complexes in methyl cyanide solution are represented in Fig. 2, where equivalent conductance (Λ_e) is plotted against $\sqrt{C}$ (C = concentration). The conductivity of $Co(ClO_4)_2 \cdot 2TTDA$ is approximately that of a 2 : 1 electrolyte. The other complexes are all weak electrolytes. The conductivity of tetrabutylammonium perchlorate—a typical strong electrolyte—is plotted for comparison. The degrees of ionization of $CoI_2 \cdot TTDA$ and $Co(NO_3)_2 \cdot TTDA$ are markedly greater than the others.

Infrared Spectra

The carbonyl stretch frequencies of all the complexes are lowered by approximately 30 cm^{-1}(TTDA) and 45 cm^{-1}(DTDA) respectively from those observed in the free ligands (1645 cm^{-1} for TTDA and 1665 cm^{-1} for DTDA). This indicates that both carbonyl oxygen atoms coordinate to cobalt(II) in all the complexes. An increase of about 20 cm^{-1} and simultaneous reduction in intensity upon complexation of the S–CH_2 wagging mode in all the complexes are interpreted as indicating coordinated sulphur atoms in the solid compounds, similar to the copper(II) complexes[1]. In the thiocyanato complexes both ν_1 (2,070 cm^{-1}) and ν_2 (480 cm^{-1}) are found in the region expected[4]

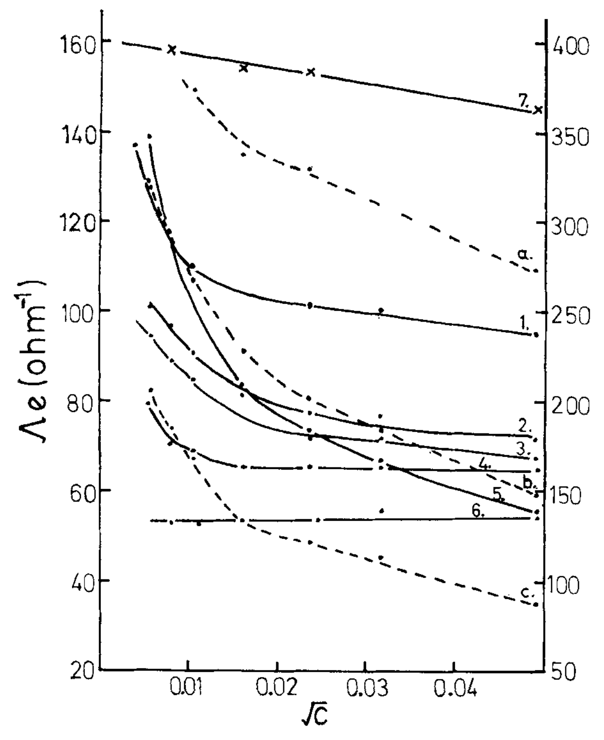

FIGURE 2 Conductivities of complexes in methyl cyanide.

1. $Co(NCS)_2 \cdot DTDA$
2. $CoBr_2 \cdot TTDA$.
3. Co $(NCS)_2 \cdot TTDA$.
4. $CoCl_2 \cdot TTDA$.
5. $Co(NO_3)_2 \cdot DTDA$
6. $CoCl_2 \cdot DTDA$.
7. Tetrabutylammonium perchlorate.

a. $Co(ClO_4)_2 \cdot 2TTDA$
b. $CoI_2 \cdot TTDA$.
c. $Co(NO_3)_2 \cdot TTDA$.

Letter symbols refer to right-hand abscissa.

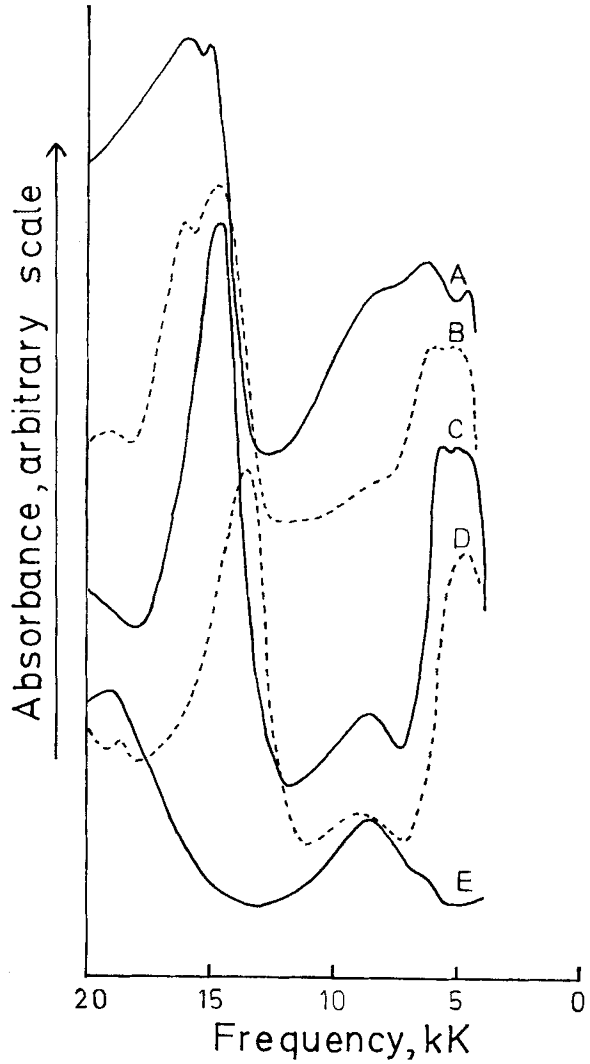

FIGURE 3 Solid reflectance elctronic spectra of complexes.

A. $Co(NO_3)_2 \cdot TTDA$.
B. $CoCl_2$.TTDA
C. $CoBr_2 \cdot TTDA$
D. $CoI_2 \cdot TTDA$.
E. $Co(NO_3)_2 \cdot DTDA$.

for N-bonded thiocyanate. A symmetrical peak at $1075\ \text{cm}^{-1}$ in the perchlorate complex was assigned to ionic perchlorate. Although nitrate vibrations were somewhat obscured by ligand vibrations covalent nitrato peaks could be observed at about $1290\ \text{cm}^{-1}$ and $1460\ \text{cm}^{-1}$ in both nitrato complexes.

Electronic Spectra and Structure

A close relationship exists between the shape and structure of the solid reflectance electronic spectra of the halo complexes of TTDA as well as their corresponding DTDA complexes. (See Fig. 3.) These spectra very closely resemble those of β-$CoX_2 \cdot$paphy[5] ($X = Cl^-$ or Br^- and paphy = pyridine-2-aldehyde-2′-pyridyl-hydrazone) and $CoCl_2 \cdot$terpy (terpy = 2,2′,2″-terpyridyl). (See Fig. 4.)

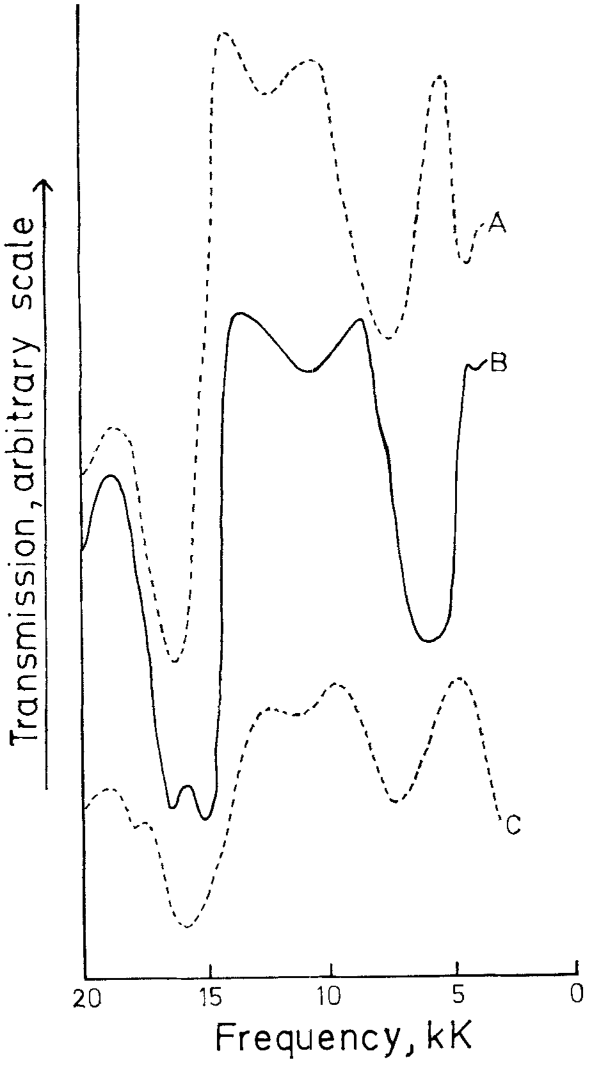

FIGURE 4 Comparison of penta-coordinate solid reflectance spectra.

A. $CoCl_2 \cdot$paphy. C. $CoCl_2 \cdot$Terpy.
B. $CoCl_2 \cdot$TTDA.

Crystal structure determinations of both $CoCl_2 \cdot$paphy[5a] and $CoCl_2 \cdot$terpy[6] proved them to have very similar distorted penta-coordinated structures, almost exactly between those of square pyramidal and trigonal bipyramidal. The structure of β-$CoCl_2 \cdot$paphy is slightly closer to C_{4v} symmetry whereas $CoCl_2 \cdot$terpy is slightly closer to D_{3h} symmetry.[6] In the light of the similarity of the electronic spectra of these with that of $CoCl_2 \cdot$TTDA as well as the fact that $CuCl_2 \cdot$TTDA was proved to be a distorted square pyramid, it is assumed that the structure of the $CoX_2 \cdot$TTDA complexes (X = halide) will be closely related to that of $CoCl_2 \cdot$paphy. Tentative assignments of peaks were, therefore, made in terms of C_{4v} symmetry.

Gaussian analysis[2] of the solid reflectance spectra (where possible) were made to determine more accurate values for the electronic transitions. The results as well as the tentative assignments of the peaks are given in Table II.

The methyl cyanide solution spectra of $CoCl_2 \cdot$TTDA and $CoBr_2 \cdot$TTDA are very similar and only slightly different from the solid reflectance spectra. ϵ_M-values of the main peaks (ν_4) are about 200 and 600 respectively. The methyl cyanide solution spectrum of $CoI_2 \cdot$TTDA differs considerably from its corresponding solid spectrum. The ϵ_M-value of ν_4 is reduced to about 120 and a peak at about 19.2 kk (520 mμ) appears. This is also found in the very similar solution spectrum of $CoI_2 \cdot$2TTDA and is indicative of O_h cobalt(II). This fact and also its relatively greater conductivity (see Fig. 2) indicate that this solution consists of a large number of species in equilibrium.

The solid reflectance spectra of the thiocyanato complexes differ from those of the chloro complexes in that the whole spectrum is shifted towards higher energy values and that ν_3 appears to be shifted under ν_2 since a broad peak is obtained in the 10–6kk region. Although these spectra are fairly similar to the spectra of tetrahedral cobalt(II), these complexes are assumed to be penta-coordinated in the solid state as a result of the evidence from their infrared spectra which indicated OSO2N chromophores and their similarity to the spectrum

TABLE II

Electronic spectral data of complexes

	$^4A_2(F) \rightarrow {}^4B_2(\nu_1)$	$^4A_2 \rightarrow {}^4E(\nu_2)$	$^4A_2 \rightarrow {}^4B_1(\nu_3)$	$^4A_2 \rightarrow {}^4E(\nu_4)$	$^4A_2 \rightarrow {}^4A_2(P)(\nu_5)$
$CoCl_2 \cdot$TTDA	4.79[a](71)[b]	6.12(104)	8.36(45)	14.2(19) 14.7(310) 15.6(177)	17.1(615) 19.4(30) 20.8(43)
$CoBr_2 \cdot$TTDA		5.76(106)	8.74(114)	14.4(221) 15.5(29)	18.0(47) 20.9(53)
$CoI_2 \cdot$TTDA		4.65(436)	8.94(124)	13.09(81) 14.1(575)	
$CoCl_2 \cdot$DTDA		6.1(113)	7.38(297)	14.5(231)	16.2(95) 18.8(164)
$Co(NCS)_2 \cdot$TTDA		6.7(90)	8.5(5.7)	15.1(38) 15.9(310)	17.3(123) 19.6(98)
$Co(NCS)_2 \cdot$DTDA				15.89(296)	17.4(89)

[a] Maxima in kk [b] Relative oscillator strength

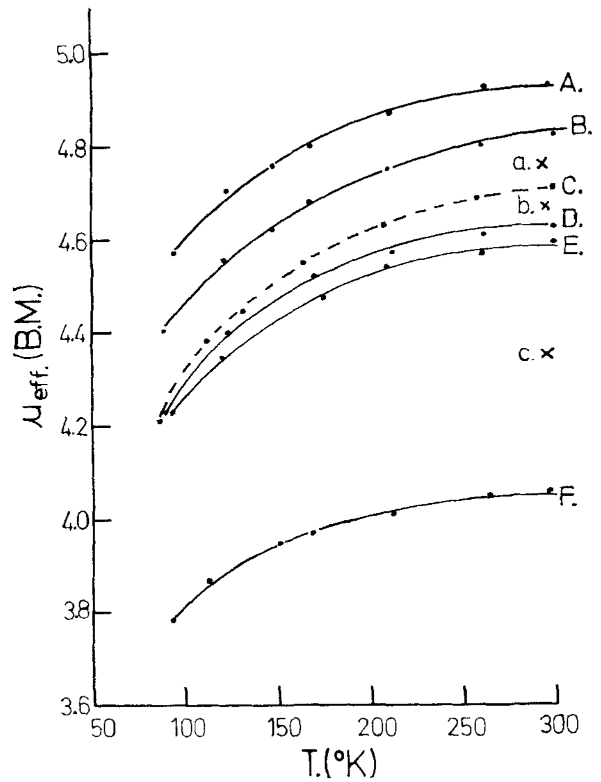

FIGURE 5 Magnetic properties of complexes.

A. $CoI_2 \cdot$TTDA D. $CoCl_2 \cdot$TTDA
B. $Co(ClO_4)_2 \cdot 2$TTDA. E. $Co(NO_3)_2 \cdot$TTDA.
C. $Co(NO_3)_2 \cdot$DTDA. F. $Co(NCS)_2 \cdot$TTDA

a, b and c represent room temperature values of $CoCl_2 \cdot$DTDA, $CoBr_2 \cdot$TTDA and $Co(NCS)_2 \cdot$DTDA respectively.

of $Co(NCS)_2$·terpy[7] which was assumed to be penta-coordinate.

The solid reflectance spectrum of the blue very hygroscopic $Co(NO_3)_2$.TTDA (See Fig. 3) is similar to that of the chloro complex and is regarded as penta-coordinated. Similar changes to that of CoI_2.TTDA take place upon dissolution in methyl cyanide indicating the presence of octahedral species in equilibrium with penta-coordinated species. Both the solid reflectance and methyl cyanide solution spectra of mauve non-hygroscopic $Co(NO_3)_2$.DTDA indicate an octahedral structure (See Fig. 3). This structural difference between the two nitrato complexes would be possible if one of the nitrato groups is bidentate in the case of the DTDA complex.

The solid reflectance and methyl cyanide solution spectra of $Co(C10_4)_2$.2TTDA, although mutually different, are both typical of octahedral cobalt(II) complexes and similar to that of $Co(NO_3)_2$.DTDA. (See Fig. 3).

Magnetic Properties

The room temperature (295°K) μ_{eff} values of all the CoX_2.TTDA and DTDA complexes discussed in this paper are given in Fig. 5. These values for the suggested penta-coordinated species vary from 4.93B.M. for the iodide (anion with weakest ligand field strength) to 4.06B.M.for the thiocyanate (anion with biggest ligand field strength). This inverse proportionality of μ_{eff} with ligand field strength as well as the temperature dependence is compatible with the magnetic behaviour of high-spin penta-coordinated cobalt(II) complexes.

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