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Studies on Some Dithiocarbamato-Bridged Heterobimetallic Complexes: Part II

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Synopsis. Some dithiocarbamato-bridged heterobimetallic complexes of the type $M^I[Zn(dtc)_3]$ and $M^{II}[Zn(dtc)_3]_2$, (M=Co(II), Ni(II), Cu(II), Pd(II), Pb(II), Cd(II), Tl(I), Ag(I), dtc=diethyldithiocarbamate), have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, (^1H, ^{13}C) NMR, UV-visible, and infrared spectral studies. The complexes are nonelectrolytes. The infrared spectral bands and NMR signals indicate the presence of only one type of dithiocarbamate group. The electronic spectra of the complexes recorded in chloroform, pyridine, and dimethyl sulfoxide are similar to their nujol mull spectra indicating no change in the geometry of the central metal. Magnetic moment, electronic spectra, and ESR studies are commensurate with a square-planar geometry around Co(II), Ni(II), Pd(II), and Cu(II).

In the previous paper,[1] the synthesis and spectroscopic studies of some novel xanthato-bridged heterobimetallic complexes of the type $M[M'(Etxant)_3]_2$ and $M[M'(Etxant)_3]$ have been reported. The ligand dithiocarbamate is closely related to xanthate, nevertheless due to replacement of oxygen with nitrogen some interesting changes in bonding behavior and reactivity of the complexes may be expected. With this viewpoint, we wish to report here the synthesis and structural studies of some analogous dithiocarbamato-bridged heterobimetallic complexes involving some transition and non-transition metal ions.

Experimental

All the chemicals used in the preparative work were BDH (AR) or equivalent grades. The solvents were freshly distilled. Sodium diethyldithiocarbamate trihydrate ($Nadtc\cdot 3H_2O$) was prepared according to literature procedure.[2] The experimental details pertaining to analysis of metals, sulfur, carbon, hydrogen, nitrogen, room-temperature magnetic susceptibility measurements, and recording of infrared and NMR spectra are same as described earlier.[1] ESR spectrum of $Cu[Zn(dtc)_3]_2$ was recorded in $CHCl_3$ on a Varian E-117 X-band spectrophotometer using DPPH (g=2.00277) as a g marker at room temperature.

Preparation of the Complexes: $Na[Zn(dtc)_3]$ required for the synthesis of $M[Zn(dtc)_3]$ and $M[Zn(dtc)_3]_2$ was prepared[3] in situ by adding 25 cm^3 acetone solution of zinc acetate (1 mmol, 0.220 g) to 40 cm^3 acetone-water mixture 90 : 10 (v/v) solution of $Nadtc\cdot 3H_2O$ (3 mmol, 0.675 g). To the above $Na[Zn(dtc)_3]$ solution, 25 cm^3 solution (1 mmol or 0.5 mmol) of $AgNO_3$ (0.17 g), Tl_2SO_4 (0.12 g), $CoCl_2\cdot 6H_2O$ (0.12 g), $NiCl_2\cdot 6H_2O$ (0.12 g), $CuSO_4\cdot 5H_2O$ (0.12 g), $Pb(NO_3)_2$ (0.16 g), $CdSO_4$ (0.15 g), or K_2PdCl_4 (0.16 g) dissolved in acetone-water 80 : 20 (v/v) was added gradually with constant stirring. All the heterobimetallic complexes which precipitated as fine crystalline material were filtered, washed with acetone-water 50 : 50 (v/v) mixture and dried in vacuum.

Results and Discussion

The analytical results (Table 1) indicate the formation of heterobimetallic complexes of the types $M[Zn(dtc)_3]$ and $M[Zn(dtc)_3]_2$ by the metathetic reaction of $Na[Zn(dtc)_3]$ and the corresponding metal salts in an appropriate molar ratio. The heterobimetallic complexes do not melt but decompose in the temperature range 165—225 °C. They are insoluble in water but soluble in most of the common organic solvents such as methanol, benzene, chloroform, *N,N*-dimethylformamide, dimethyl sulfoxide, and pyri-

Table 1. Analytical Data, Magnetic Moment, and Molar Conductance of Heterobimetallic Dithiocarbamates

Complex	Color	Mp/Decomp[b] temp	Found (Calcd)/%						μ_{eff}	Molar coductance[a]
		°C	Zn	M	S	C	H	N	BM	
$Ni[Zn(dtc)_3]_2$	Light green	174(d)	12.30 (12.14)	5.8 (5.5)	36.12 (35.65)	33.80 (33.41)	5.74 (5.56)	7.66 (7.79)	Diamag.	1.58
$Co[Zn(dtc)_3]_2$	Green	225(d)	12.43 (12.14)	5.38 (5.47)	35.02 (35.66)	33.90 (33.40)	5.42 (5.56)	7.60 (7.79)	2.03	6.89
$Cu[Zn(dtc)_3]_2$	Brown	180(d)	11.93 (12.09)	5.43 (5.87)	30.83 (31.32)	33.08 (33.26)	5.47 (5.54)	7.38 (7.76)	2.23	1.35
$Ag[Zn(dtc)_3]$	Sky blue	165(d)	10.25 (10.59)	18.02 (17.49)	30.96 (31.10)	29.46 (29.15)	4.68 (4.85)	6.56 (6.80)	—	—
$Tl[Zn(dtc)_3]$	Dirty white	176(d)	8.56 (9.16)	29.01 (28.63)	26.03 (26.89)	24.58 (25.21)	4.43 (4.20)	5.98 (5.88)	—	2.14
$Pb[Zn(dtc)_3]_2$	Dirty white	166(d)	10.93 (10.67)	17.24 (16.90)	30.09 (31.32)	28.57 (29.36)	5.01 (4.89)	6.57 (6.85)	—	1.01
$Cd[Zn(dtc)_3]_2$	Dirty white	205	11.93 (11.56)	10.09 (9.93)	34.26 (33.94)	32.02 (31.82)	5.60 (5.30)	7.69 (7.42)	—	1.58
$Pd[Zn(dtc)_3]_2$	Yellow	173(d)	— (11.64)	— (9.29)	— (34.19)	29.43 (32.06)	5.04 (5.34)	6.39 (7.42)	—	2.56

a) In methanol. b) (d) Decomposition temp.

dine. The very low molar conductance values (1.01—6.89 S cm^2 mol^{-1}) in methanol are indicative of their nonelectrolytic nature.[4]

The magentic moment value of 2.03 BM and electronic spectral bands at 7000, 11400, 15600, and 20000 cm^{-1} for Co[Zn(dtc)$_3$]$_2$ suggest square-planar geometry around Co(II). The first and third bands are assigned to $^2A_{1g}\rightarrow{}^2E_{1g}$ and $^2A_{1g}\rightarrow{}^2E_{2g}$ transitions, respectively.[1] The most characteristic band at 11400 cm^{-1} for square-planar Co(II) complex gives the value of B=760 cm^{-1}.

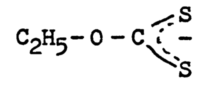
The magnetic moment value of 2.23 BM for Cu[Zn(dtc)$_3$]$_2$ corresponds to one unpaired electron. Three bands at ca. 13600, ca. 14900, and ca. 21700 cm^{-1} in the visible region spectrum of this complex are assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions in a square planar geometry[5,6] around Cu(II). The room-temperature ESR spectrum of Cu[Zn(dtc)$_3$]$_2$ in chloroform which gives the parameters $g_{\|}$=2.02, $g_{\perp}$=2.02, and g_{av}=2.02, together with the electronic spectral bands, indicate a four coordinate square-planar Cu(II) species.

The diamagnetic nature of Ni[Zn(dtc)$_3$]$_2$ and occurrence of bands at ca. 15900 and ca. 20400 cm^{-1} suggest square planar geometry around Ni(II). The latter absorption bands may be assigned to $^1A_{1g}\rightarrow{}^1B_{1g}$ and $^1A_{1g}\rightarrow{}^1A_{2g}$ transitions,[1] respectively. The value of the ligand field paremeter, Δ_1=18700 cm^{-1}, places the dithiocarbamate after xanthate in the spectrochemical series in a planar NiS$_4$ environment.

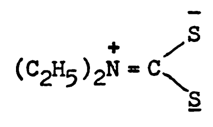
As expected Pd[Zn(dtc)$_3$]$_2$ complex is diamagnetic and exhibits a band at 22900 cm^{-1} which may be assigned to metal-ligand charge transfer. As compared to Ni(II) complexes, the first spin-allowed d-d transition in the Pd(II) complex is expected to occur at higher energy but it is generally not observed probably because it is masked by the tail of the following charge-transfer band.

In order to study the Lewis acid behavior, the heterobimetallic complexes containing Co(II), Ni(II), Pd(II), or Cu(II) as one of the metal ions have been dissolved in some coordinating as well as non-coordinating solvents like dimethyl sulfoxide, pyridine, chloroform and their UV-visible spectra were studied. The electronic spectral pattern of the complexes is almost similar to their nujol mull spectra, indicating no change in the geometry of the central metal and ruling out the possibility of ligand coordination to cobalt, nickel, palladium, or copper. M[Zn(dtc)$_3$]$_2$ [M=Ni(II), Co(II), or Cu(II)] complexes are quite insensitive to axial perturbation and their electronic spectra in donor solvents such as pyridine remain unchanged. In general NiS$_4$ complexes vary substantially in their ability to interact with Lewis bases. This tendency is closely related to the change in the electronic properties of the ligand as a whole rather than to the donor atoms alone. Thus xanthate,[7] dithiophosphate[8] complexes interact strongly, while dithiocarbamate complexes are generally unperturbed similar to the 1,2-dithiolene complexes[9] by dissolution in strong donor solvents such as pyridine. The reluctance of dithiocarbamate complexes to undergo axial interaction has been rationalized[2,10] by considering that sulfur atoms can donate electrons of π-symmetry into a nonbonding MO containing 4p$_z$ function of the nickel ion. Any strong π-interaction of this kind should decrease the availability of the 4p$_z$ orbital for interaction with bases. Thus the behavior of NiS$_4$ in this context suggests substantial S$\rightarrow$Ni π-bonding and that the π-bonding increases in the order dithiophosphates$\approx$xanthates$<$dithiocarbamates$<$dithiolene. This is also because, resonance form (b) is more dominating in dithiocarbamate complexes similar to dithiolene while resonance form (a) is dominating in case of binary metal xanthates. Electronic spectra of these complexes as nujol mull are almost similar to those of the analogous xanthato-bridged heterobimetallic complexes but the solution spectra show the absence of ligand-metal interaction.

The infrared spectra of all the heterobimetallic complexes studied over the region 4000—200 cm^{-1} (Table 2) are very similar and have been assigned on the basis of earlier studies.[2] The thioureide bands occurring at 1445—1460 cm^{-1} are attributed to the CN stretching vibration of the S$_2$C-NC$_2$H$_5$ bond. This band is in the midway of ν(C-N) (1250—1350 cm^{-1}) and ν(C=N) (1640—1690 cm^{-1}) and shows an increase in the double bond character of the C-N bond thereby justifying the major contribution of resonance form (b) for



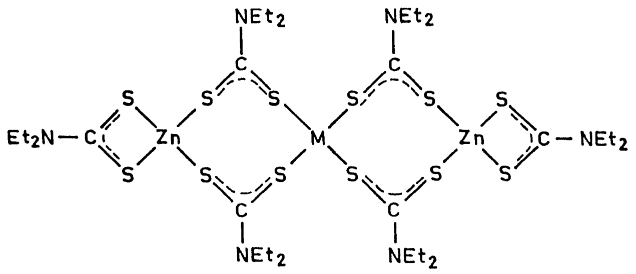
(a)



(b)

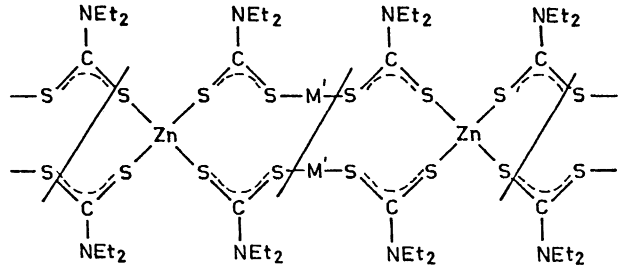
Table 2. Selected Infrared Spectral Bands (cm^{-1}) and ^{1}H and ^{13}C Chemical Shifts of the Complexes

Complexes	ν(C=N)	ν(C$\doteq$S)	^{1}H		^{13}C	
			$-C\underline{H}_3$	$-C\underline{H}_2$	$\underline{C}H_3$	$\underline{C}H_2$
Ni[Zn(dtc)$_3$]$_2$	1460	1070, 1095	1.24(t)	3.62(q)	12.40	43.77
Co[Zn(dtc)$_3$]$_2$	1455	990, 975	1.27(q)	3.77(m)	12.13 12.56	42.74 49.24
Cu[Zn(dtc)$_3$]$_2$	1460	1070, 1090	1.20	3.87	—	—
Ag[Zn(dtc)$_3$]	1445	990, 970				
Tl[Zn(dtc)$_3$]	1455	1070, 1090	1.33(t)	3.84(q)	12.14	49.20
Pd[Zn(dtc)$_3$]$_2$	1450	1070, 1095	1.33(t)	3.84(q)	12.20	48.44
Cd[Zn(dtc)$_3$]$_2$	1455	1070, 1095	1.34(t)	3.84(q)	12.13	49.89
Pd[Zn(dtc)$_3$]$_2$	1450	1070, 1090	1.32(5)	3.77(q)	12.40	49.24



M = Co(II), Ni(II), Cu(II), Pb(II), Cd(II), Pd(II)

1. M$[\mathrm{Zn(dtc)_3}]_2$



M' = Ag(I), Tl(I)

2. M'$[\mathrm{Zn(dtc)_3}]$

Fig. 1.

dithiocarbamate complexes. The two bands occurring in the region 990—1070 and 970—1095 cm^{-1} are associated with $\nu(\mathrm{C{\overset{\cdots}{-}}S})$ vibrations, indicating unsymmetrical bidentate/bridging behavior of the dithiocarbamate moiety linked to two different metal centers. The bands observed below 400 cm^{-1} are due to metal-sulfur stretching vibrations.

^{1}H NMR spectra of the complexes (Table 2) exhibit signals due to -CH$_3$ and -CH$_2$ protons[10] around δ=1.24—1.34 and 3.62—3.84 in the intensity ratio of 3 : 2 which are in between monodentate and bidentate dithiocarbamate. This may be probably due to the bridging/unsymmetrical bidentate behavior of dithiocarbamate linked to two different metal centers. The downfield shift observed in -CH$_3$ protons and the upfield shift in -NCH$_2$ protons as compared to sodium dithiocarbamate indicate the deshielding of -CH$_3$ protons and shielding of -NCH$_2$ protons in these complexes. For Co[Zn(dtc)$_3$]$_2$ the increased number of peaks for -CH$_3$ and -NCH$_2$ protons is due to the presence of paramagnetic Co(II) and diamagnetic Zn(II) centers. However, in the case of Cu[Zn(dtc)$_3$]$_2$, the -CH$_3$ and -NCH$_2$ protons show broad signals because of the presence of paramagnetic Cu(II) center.

^{13}C NMR spectra of the diamagnetic complexes show two signals at δ=12.13—12.4 and 43.77—49.89 corresponding to -$\underline{\mathrm{C}}\mathrm{H_3}$ and -N$\underline{\mathrm{C}}\mathrm{H_2}$ carbons respectively and suggest the intermediate behavior (unidentate and bidentate) of dithiocarbamate attached to two metal centers. Each of these signals shows splitting for Co[Zn(dtc)$_3$]$_2$ indicating the presence of two types of -N$\underline{\mathrm{C}}\mathrm{H_2}$-$\underline{\mathrm{C}}\mathrm{H_3}$ carbons due to the presence of unpaired electron of Co(II).

On the basis of these studies the complexes are expected to have structures similar to the xanthato-bridged heterobimetallic complexes[1] (Fig. 1).

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