The Syntheses and Properties of Cobalt(II), Nickel(II) and Copper(II) Complexes with some Heterocyclic Dithiocarbamates

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New cobalt(II), nickel(II) and copper(II) dithiocarbamato complexes of the type M(Rdtc)$_2$ (Rdtc = 4-phenylpiperidinedithiocarbamate and N-phenylpiperazinedithiocarbamate) have been prepared and characterized through elemental analyses, conductivity measurements, spectral (electronic and IR) studies, magnetic moment measurements at different temperatures, e.p.r. techniques and thermal analyses (TG and DTG). The dithioligands exhibit bidentate behaviour in all the complexes. The magnetic moments studies suggest that there is no significant interaction between copper ions, and the e.p.r. data provide parameters typical of sulphur coordination in planar CuS$_4$ chromophores.

Introduction

Working on the coordinating behaviour of the heterocyclic containing dithiocarbamate ligands and on the reactivity of their coordination compounds, we report in this study the preparation and characterization of new complexes of cobalt(II), nickel(II) and copper(II) with 4-phenylpiperidine- and N-phenylpiperazinedithiocarbamate
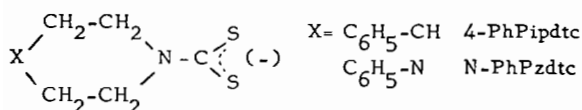
We have previously described the complexes of cyclic dithiocarbamates (X = CH$_2$, O, S, NH, N-CH$_3$) with many d- and p-block metals [1–12]. The reactivity of the complexes obtained towards bidentate nitrogen donor ligands, the mass spectral investigations and the structural characterization by XPS techniques have been investigated and some preliminary results already reported [10, 13–16].

This paper extends previous studies on the dithiocarbamates in which dialkyl groups are replaced by heterocycles. It is of interest to study the influence of the different heterocyclic groups (bearing a phenyl group in the same position but linked to a different atom of the ring) on the C$\doteq$N and C$\doteq$S bonds and on the electronic structure of the complexes. The nature of the heterocycle influences the behaviour of the dithiocarbamate ligands through variation in the electron releasing ability of the different amines.

Experimental

Preparation of the Ligands

The sodium salts of the ligands were prepared by treating 4-phenylpiperidine (reagent grade) in dry ethyl ether and isopropyl alcohol and N-phenylpiperazine (reagent grade) in dry ethyl ether with CS$_2$ and adding NaOH with vigorous stirring over a 5 h period. Molar ratios amine: CS$_2$: NaOH = 1:1:1. The crude products were recrystallized from isopropyl alcohol or acetone. *Anal.* Calc. for C$_{12}$H$_{14}$NS$_2$-Na·2H$_2$O: C, 48.8; H, 6.1; N, 4.7. Found: C, 48.3; H, 6.1; N, 4.8%. Calc. for C$_{11}$H$_{13}$N$_2$S$_2$Na·2H$_2$O: C, 44.6; H, 5.8; N, 9.5. Found: C, 44.7; H, 5.6; N, 9.5%.

Preparation of the Complexes

The complexes were obtained by reaction of the metal chloride in aqueous solution with water/methanol solutions of the dithiocarbamate sodium salt, in a 1:2 metal:ligand molar ratio. The compounds which precipitated immediately were washed several times with cold water and dried over P$_4$O$_{10}$.

We have obtained compounds only with the metal: ligand ratios reported in the Table I; repeated syntheses and elemental analyses gave reproducible results.

Infrared Measurements

The IR spectra were recorded in the 4000–50 cm^{-1} region with a Perkin-Elmer 180 spectrophotometer of the Instruments Centre of Modena University. The spectra in the 4000–400 cm^{-1} region were measured as KBr discs or Nujol mulls. Far-IR spectra were measured on Nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen.

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TABLE I. Electronic and Infrared Spectra (cm^{-1}) and Magnetic Data.[a]

Compounds	d–d bands			$\nu(C \doteq N)$	$\nu(C \doteq S)$	$\nu(M-S)$	$\delta(M-S)$ + ring vibrations	μ B.M.
Co(4-PhPipdtc)$_2 \cdot$0.5H$_2$O	8300, 15700, 20800, 25000			1485vs	965ms	356ms	244mw	2.30
Co(N-PhPzdtc)$_2 \cdot$0.5H$_2$O	8600, 15700, 20000, 25000			1490vs	990m	355ms	245m	2.14
	ν_1	ν_2	ν_3					
Ni(4-PhPipdtc)$_2$	16300	20400	23100, 25600	1494vs	951m	387ms	250m	dia.
Ni(N-PhPzdtc)$_2$	16100	20400	23300, 25800	1490vs	990m	387m	250m	dia.
	ν_1	ν_3						
Cu(4-PhPipdtc)$_2$	14800	21500		1490vs	952m	356ms	282vs	1.73
Cu(N-PhPzdtc)$_2$	14900	21400		1480ms	985m	353ms	284ms	1.73

[a]4-PhPipdtcNa: $\nu(C \doteq N)$ 1469vs; $\nu(C \doteq S)$ 958ms; N-PhPzdtcNa: $\nu(C \doteq N)$ 1465s; $\nu(C \doteq S)$ 975m.

Electronic Spectra

The electronic spectra were recorded with a Shimadzu MPS-50L spectrophotometer in the solid state in the 8000–40000 cm^{-1} region. Samples were prepared by grinding the complexes on a filter paper as support.

E.p.r. Spectra

The e.p.r. spectra of the copper complexes were recorded at X-band frequencies on a Varian E-9 spectrometer at liquid N$_2$ temperature; the samples were doped (1:100) in the nickel(II) analogous complexes.

Magnetic Measurements

These measurements were carried out at room temperature by Gouy's method. Molecular susceptibilities were corrected for diamagnetism of the component atoms by use of Pascal's constants. In the case of the copper(II) derivatives, magnetic susceptibilities were measured in a nitrogen atmosphere by the absolute Gouy's method over the 120–300 K range; the measurements were made in 1500 gauss intervals up to 6000 gauss, at each temperature. The samples were kept at each temperature for 30 minutes before the readings. The variable temperature unit is a Gouy Balance MkII of the Newport Instruments Ltd. The standardization was performed with Hg[Co(SCN)$_4$] and the molar susceptibilities were corrected for diamagnetism by using the Pascal constants.

Thermal Analyses

Thermogravimetric analyses (TG and DTG) were performed in air on a Mettler TG50 thermobalance equipped with a Mettler TC10TA processor. A scan rate of 10 °C min^{-1} was used.

Conductivity Measurements

These measurements were carried out with a WTW LBR type conductivity bridge for freshly prepared 10^{-3} M solutions in DMF at 25 ± 0.1 °C.

Analyses

Carbon, nitrogen and hydrogen were determined using a Carlo Erba 1106 elemental analyzer.

Results and Discussion

All the complexes whose elemental analyses gave satisfactory results are listed in the Table I, together with the pertinent IR data in the 4000–50 cm^{-1} region (i.e. $\nu(C \doteq N)$, $\nu(C \doteq S)$, $\nu(M-S)$ and $\delta(M-S)$ and ring deformation coupled bands), the principal features of the electronic spectra and the magnetic moment values; the e.p.r. data are given in the Table II, while the thermogravimetric studies are presented in Table III.

The compounds are microcrystalline or powder-like, stable in atmospheric conditions, soluble in acetone, methanol, ethanol, benzene and N,N'-dimethylformamide (DMF); conductivity measurements in this last solvent show that the complexes are covalent and that ionic species are absent in solution.

TABLE II. E.p.r. Data of Copper(II) Complexes.

Parameter	Cu(4-PhPipdtc)$_2$	Cu(N-PhPzdtc)$_2$
$g_{\parallel}$	2.081	2.085
$g_{\perp}$	2.024	2.026
$\bar{g}$	2.043	2.046
$A_{\parallel}(^{63}Cu)$	159	158
$A_{\parallel}(^{65}Cu)$	170	169
$A_{\perp}$	44	44
α	0.67	0.68

TABLE III. Thermal Analyses Data.

| Compounds	Observed and (calculated) weight losses %			
	H_2O	I° step	II° step	III° step
Co(4-PhPipdtc)$_2$·0.5H$_2$O	1.87(1.69)	70.07(69.65)	13.57(13.52)	2.95(2.96)
Co(N-PhPzdtc)$_2$·0.5H$_2$O	1.98(1.69)	70.68(69.76)	14.81(13.47)	3.43(2.96)
Ni(4-PhPipdtc)$_2$		69.42(69.16)	14.43(13.76)	3.85(3.01)
Ni(N-PhPzdtc)$_2$		70.02(69.28)	13.38(13.71)	3.95(3.01)
Cu(4-PhPipdtc)$_2$		72.95(73.20)	8.88(8.97)	3.21(3.00)
Cu(N-PhPzdtc)$_2$		77.69(77.77)	8.45(7.45)	

Infrared Spectra

The IR spectra of the ligands and their metal complexes are given in Table I. The presence of the thioureido band near 1500 cm^{-1} suggests a considerable double bond character in the C$\doteq$N bond; this fact can be attributed to the electron releasing ability of the heterocyclic group which forces high electron density towards the sulphur atoms, *via* the π system, producing greater double-bond character in the carbon–nitrogen bond whose stretching vibration as a consequence increases.

All the dithiocarbamato metal derivatives reported here show bands assigned to ν(C$\doteq$N) in the 1495–1472 cm^{-1} range, which lie between ν(C=N) and ν(C–N), in the 1690–1640 and 1350–1250 cm^{-1} ranges respectively.

The bands present in the 990–951 cm^{-1} range are attributed to the prevailing contribution of ν(C$\doteq$S) [1–13, 17]. The ν(C$\doteq$S) value indicates that the dithioligands act as bidentate, in fact only one strong band is present, whereas a doublet is expected in the 1000 ± 70 cm^{-1} region in the case of monodentate coordination [18–21]. The analysis of the position of the ν(C$\doteq$N) mode gives further confirmation of such behaviour; this band, in fact, undergoes blue shifts in all the complexes, while for unidentate coordination the frequency of this stretching mode would undergo downward shifts or remain unchanged at the same value as for the free dithiocarbamate sodium salt [22].

By comparing the stretching values of the carbon–nitrogen bond with those of the previously reported complexes, we observed that the upward shift of ν(C$\doteq$N) on passing from the sodium salts to their metal complexes is lower in the case of dithiocarbamate ligands bearing a phenyl group in 4-position. This fact may be explained by taking into account the inductive effect of the phenyl group which causes a decrease in the carbon-nitrogen bond order.

The structure of the dithioligands can be represented by the following formalism
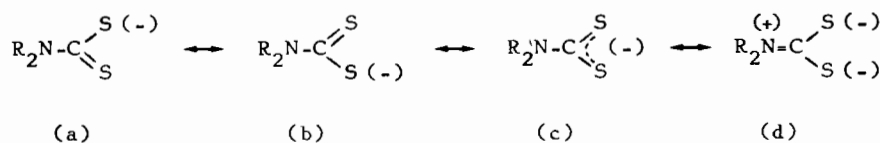
and we can suggest according to our previous studies that the contribution of the structure (d), greatest for the dialkylderivatives, lower for more complex aliphatic chains and relatively small for the heterocyclic derivatives, is smaller for the compounds reported here owing to the presence of the phenyl ring.

In the far-IR region the bands of the ligands are unchanged in the spectra of the complexes; in addition new bands, absent in the spectra of the starting materials, are observed in the 387–353 and 284–244 cm^{-1} ranges. The band between 387 and 353 cm^{-1} is due to ν(M–S) stretching modes, whereas the other band could be attributed to complex normal modes involving both metal–sulphur bond and ring vibration modes [23].

E.p.r. and Electronic Spectra and Magnetic Measurements

In the e.p.r. spectra of the copper complexes doped (1:100) in the nickel(II) homologues recorded at liquid N$_2$ temperature, the characteristic splittings of the ^{63}Cu and ^{65}Cu isotopes were observed in the 3:1 ratio [11]. Figure 1 shows, as a representative example, the spectrum of the Cu(4-PhPipdtc)$_2$ complex. Computer simulation was not necessary because of the relative simplicity in positioning either $g_\parallel$ and $A_\parallel$ or $g_\perp$ and $A_\perp$ values.

The principal g values are small and typical for sulphur coordination.

The α bonding parameters for the copper complexes, Table II, have been calculated on the basis of the proposed equations [24] and the obtained values are indicative of strongly covalent metal–ligand interactions.

The $|A_\parallel|$ values, high with respect to those of a 'flattened' tetrahedral coordination [25], are of the order of those expected either for planar or for distorted octahedral sulphur containing chromophores. This last possibility must be excluded on the basis of the lack of orbital contribution to the spin
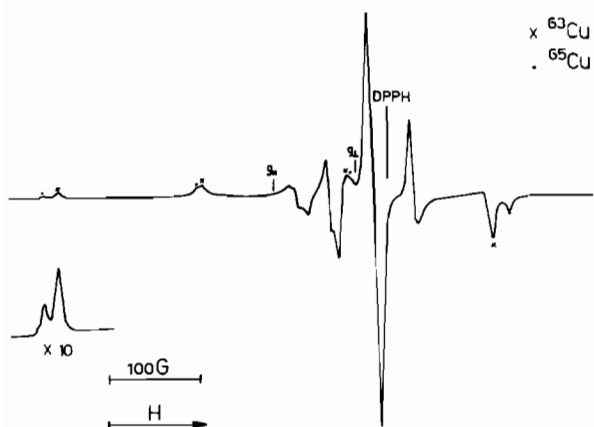
R$_2$N-C$\overset{S(-)}{\underset{S}{<}}$ ↔ R$_2$N-C$\overset{S}{\underset{S(-)}{<}}$ ↔ R$_2$N-C$\overset{S}{\underset{S}{<}}$(-) ↔ R$_2$N=C$\overset{(+)\ S(-)}{\underset{S(-)}{<}}$

   (a)   (b)   (c)   (d)

Fig. 1. E.p.r. spectrum of the Cu(4-PhPipdtc)$_2$ complex in the solid state at liquid nitrogen temperature.

Fig. 2. Curie-Weiss plots: (A) Cu(N-PhPzdtc)$_2$; (B) Cu(4-PhPipdtc)$_2$.

only value ($\mu \simeq 1.73$) and of the axial line-shape of the spectra.

The analysis of the spectra can be tested to some degree by comparison of the observed and calculated magnetic moments. Using the standard formula $\mu_{B.M.} = 1/3(g_\parallel + 2g_\perp)\sqrt{s(s+1)}$ and inserting the g values found in this work, the calculated magnetic moments (1.77 B.M. for both the copper complexes) match very well the experimental ones.

In the electronic spectra of the copper compounds two bands are found at about 15000 and 21500 cm^{-1}. They can be assigned, according to other authors [26], to the $d_{xy} \rightarrow d_{z^2}(\nu_1)$ and $d_{xy} \rightarrow d_{xz}$, $d_{yz}(\nu_3)$ transitions respectively in a D$_{2h}$ point symmetry. In addition the $g_\parallel$ and $g_\perp$ values ($g_\parallel > g_\perp$) give a confirmation that d_{xy} is the ground state.

Using the diagram of the dependance of the calculated transition energies for CuS$_4$ chromophores (d^9 electronic configuration) in a D$_{2h}$ planar symmetry on the ligand field parameter $\alpha_4{}^S$ ($\alpha_4{}^S$ = the crystal field parameter for sulphur atoms bound to copper) [26], we have found a $\alpha_4{}^S$ value of -12440 cm^{-1}, very similar to the value found by the above cited authors (-12000 cm^{-1}).

The low θ values obtained from variable temperature susceptibilities (-3.0 and -2.0 K for the 4-PhPipdtc and N-PhPzdtc complex respectively) indicate that there is none or very little interaction between copper ions in the complexes, Fig. 2.

As regards the cobalt derivatives, from spectroscopic and magnetic data we suggest a low-spin tetracoordinate planar structure. The electronic spectra exhibit characteristic ligand field bands and are remarkably different from those observed for hexacoordinate octahedral or tetracoordinate tetrahedral cobalt(II) complexes.

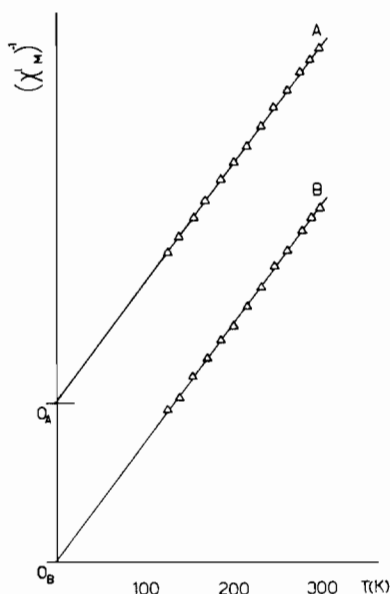The nickel(II) derivatives are diamagnetic and square planar. Three spin-allowed d–d transitions

from the $^1A_{1g}$ ground state to the excited $^1A_{2g}$, $^1B_{1g}$ and ^1E_g levels, in order of increasing energy are expected. The ν_3 is split because of the two-fold degeneracy of the ^1E_g state. The orbital parameter Δ_1, calculated from the $x^2 - y^2 \rightarrow xy$ in plane transition [27] lies in the 18900–19100 cm^{-1} range by assuming a correction factor of 2800 cm^{-1} [28] and places these ligands in the spectrochemical series of the sulphur donors.

Thermogravimetric Studies

The thermal analyses were performed either on the ligands and on the metal complexes; Table III shows the temperature ranges and the relative observed and calculated weight losses.

Both the free ligands sodium salts leave Na$_2$S$_3$ as residue, which then undergoes oxidation to Na$_2$O and/or Na$_2$SO$_4$.

The data up to 900 °C for the complexes suggest a multi-step decomposition; in the case of the copper complexes the first step leads to polysulphides (N-PhPzdtc complex: CuS$_{1.75}$; 4-PhPipdtc complex: CuS$_{2.5}$) depending on the ligand present.

The first step for the cobalt and nickel complexes, apart the water loss in the 35–115 °C range for the cobalt derivatives, leaves H$_3$C–N–C⟨S–S⟩M as residue.

The second step leaves, for all the complexes, a MS residue which is oxidized, in a third step, to MO or to a mixture of oxides.

Acknowledgements

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