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Ligand Substitution at a Hexacoordinate Centre.
Part III. Preparation and Spectroscopic Study of Co(III) Diethyldithiocarbamato Complexes Containing Ethylenediamines

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The new $[Co(Et_2dtc)_2en]BF_4$ compounds, in which Et_2dtc is N,N-diethyl-dithiocarbamate and en is ethylenediamine or variously N-substituted ethylenediamines, have been prepared and characterized. The nature of these products has been investigated by U.V.–Vis. and I.R. spectroscopy, and their stereochemistry has been assigned on the basis of pmr spectral analysis. In particular, when the N-substituted diamines have a chiral centre at the nitrogen atom upon coordination, a strong stereoselectivity seems to affect the formation of these complexes.

Introduction

We have recently reported on the reaction of $[Co_2(Et_2dtc)_5]BF_4$ with some substituted dithiooxamides as a result of an investigation on the ligand substitution at octahedrically coordinated Co(III) dithiocarbamates [1, 2]. We have now extended this work considering the reaction of the same starting complex with a series of N-substituted ethylenediamines, obtaining the new 1:1-electrolyte mixed ligand compounds having the general formula $[Co(Et_2dtc)_2en]BF_4$.

The ethylenediamines used were chosen with nearly the same acid–base dissociation constants [3, 4], but with increasing bulkiness of N-alkyl substituents, in order to investigate the effect of the substituents on the kinetics of the reaction (see Part IV) and on the properties of the final products. In particular, since the alkyl groups substituted to diamines are capable of affecting the stereochemistry of metal complexes, we have studied the pmr spectra of these compounds in order to obtain information about their stereochemistry.

TABLE I. Analytical data. Found (calcd).[a]

	C%	H%	N%
$[Co(Et_2dtc)_2H_2enH_2]BF_4$	28.6(28.69)	5.5(5.62)	11.0(11.15)
$[Co(Et_2dtc)_2HMeenH_2]BF_4$	29.8(30.23)	5.9(5.86)	10.9(10.85)
$[Co(Et_2dtc)_2HEtenH_2]BF_4$	31.0(31.70)	6.0(6.08)	10.5(10.56)
$[Co(Et_2dtc)_2HPrenH_2]BF_4$	33.6(33.09)	6.1(6.29)	10.3(10.29)
$[Co(Et_2dtc)_2HisoPrenH_2]BF_4$	32.5(33.09)	6.1(6.29)	10.1(10.29)
$[Co(Et_2dtc)_2HMeenMeH]BF_4$	30.7(31.70)	6.3(6.08)	10.7(10.56)
$[Co(Et_2dtc)_2HEtenEtH]BF_4$	34.9(34.41)	6.5(6.50)	9.9(10.03)
$[Co(Et_2dtc)_2Me_2enMe_2]BF_4$	34.0(34.41)	6.8(6.50)	10.0(10.03)

[a] All compounds were obtained as green microcrystalline solids and they gave molar conductivities ranging around 85 ohm^{-1} cm^2 in 10^{-3} *M* solutions of CH_3NO_2 at 25 °C, characteristic of 1:1 electrolytes.

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TABLE II. Electronic Spectral Data in CH_2Cl_2, kK (log ϵ).

$[Co(Et_2dtc)_2H_2enH_2]BF_4$	41.7(4.70); 38.5sh; 35.2(4.27); 31.2(4.36); 28.6sh; 23.0sh; 17.6(2.53)
$[Co(Et_2dtc)_2HMeenH_2]BF_4$	41.3(4.46); 38.8sh; 35.0(4.18); 31.1(4.31); 28.6sh; 23.8sh; 17.5(2.56)
$[Co(Et_2dtc)_2HEtenH_2]BF_4$	41.3(4.52); 38.6sh; 35.0(4.23); 31.2(4.46); 28.7sh; 23.4sh; 17.5(2.53)
$[Co(Et_2dtc)_2HPrenH_2]BF_4$	41.5(4.44); 38.8sh; 35.0(4.25); 31.0(4.28); 28.8sh; 23.8sh; 17.4(2.50)
$[Co(Et_2dtc)_2HisoPrenH_2]BF_4$	41.2(4.56); 38.5sh; 35.0(4.32); 30.9(4.40); 28.6sh; 23.3sh; 17.3(2.55)
$[Co(Et_2dtc)_2HMeenMeH]BF_4$	41.2(4.56); 38.5sh; 35.0(4.33); 31.0(4.39); 28.6sh; 23.3sh; 17.1(2.59)
$[Co(Et_2dtc)_2HEtenEtH]BF_4$	41.2(4.50); 39.2sh; 34.8(4.27); 31.0(4.35); 28.7sh; 23.8sh; 16.9(2.55)
$[Co(Et_2dtc)_2Me_2enMe_2]BF_4$	40.5(4.50); 38.5sh; 34.8(4.24); 30.5(4.31); 28.7sh; 21.3sh; 16.3(2.66)

TABLE III. Proton Chemical Shifts δ^a (ppm) for $[Co(Et_2dtc)_2en]BF_4$ in $CDCl_3$.

en	Et_2dtc fragment		Diamine ring					
	$CH_2{}^b$	$CH_3{}^b$	$CH_2{-}CH_2{}^c$	CH_3	CH_2	CH	NH	
							$H(1,3)^d$	$H(2,4)^d$
H_2enH_2	3.66	1.28	2.95	–	–	–	$–^f$	1.57
Me_2enMe_2	3.66	1.22	2.69	2.45; 2.14	–	–	–	–
HMeenMeH	3.59	1.21	2.92 2.44	2.19^e	–	–	2.4^f	–
HEtenEtH	3.68	1.29	3.13 2.52	1.29	3.68^f	–	1.89	–
$HMeenH_2$	3.66	1.26	2.99	2.29^e	–	–	2.36	1.65
$HEtenH_2$	3.55	1.27	2.99	1.18	3.43	–	$–^f$	1.30
$HPrenH_2$	3.50	1.26	2.82	0.91^g	$2.38^\beta; 1.56^\alpha$	–	1.88	$–^h$
$HisoPrenH_2$	3.63	1.26	2.84	1.26^i; 1.07	–	3.28	$–^h$	1.38

[a] Measured at the middle point of the resonances. [b] $J_{CH_3-CH_2} = 7.0$ Hz. [c] For the features of these resonances see also Fig. 1 and related discussion. [d] These resonances were attributed tentatively in analogy with methyl attribution (see discussion) of N-substituted ethylenediamines (refer to Fig. 4). [e] $J_{CH_3-NH} = 5.7$ Hz. [f] Overlapping peak. [g] $J_{CH_3-CH_2} = 6.4$ Hz. [h] Not observed. [i] $J_{CH_2-CH} = 6.3$ Hz.

Experimental

Reagents

Ethylenediamines were Fluka Reagent Grade and were used after column distillation. They were: ethylenediamine = H_2enH_2; N-methyl-ethylenediamine = $HMeenH_2$; N-ethyl-ethylenediamine = $HEtenH_2$; N-n-propyl-ethylenediamine = $HPrenH_2$; N-iso-propyl-ethylenediamine = $HisoPrenH_2$; N,N′-dimethyl-ethylenediamine = HMeenMeH; N,N′-diethyl-ethylenediamine = HEtenEtH; N,N,N′,N′-tetramethyl-ethylenediamine = Me_2enMe_2.

Complexes

The complexes were prepared analogously as described in Part I for the dithio-oxamide derivatives [1], using the above ethylenediamines instead of the dithio-oxamides.

Measurements

C, H, N elemental analyses were performed by the Istituto di Farmacia, Università di Cagliari.

Conductivity measurements were carried out using a WTW LBR type instrument.

Infrared spectra were recorded with a Perkin-Elmer mod. 325 spectrophotometer, and U.V.–Visible spectra were carried out in CH_2Cl_2 solutions with a Perkin-Elmer mod. 402 spectrophotometer.

The ^1H NMR spectra were run at 30 °C on a Varian FT-80A spectrometer operating at 80 MHz. The variable temperature measurements were carried out using a home-made temperature control unit. The spectra were run either in $CDCl_3$ with an internal reference of tetramethylsilane (TMS) or in Me_2SO-d_6. All the deuterated solvents were purchased from Merck.

Results and Discussion

Analytical data and molar conductivities are consistent with a $[Co(Et_2dtc)_2en]BF_4$ formulation (see Table I).

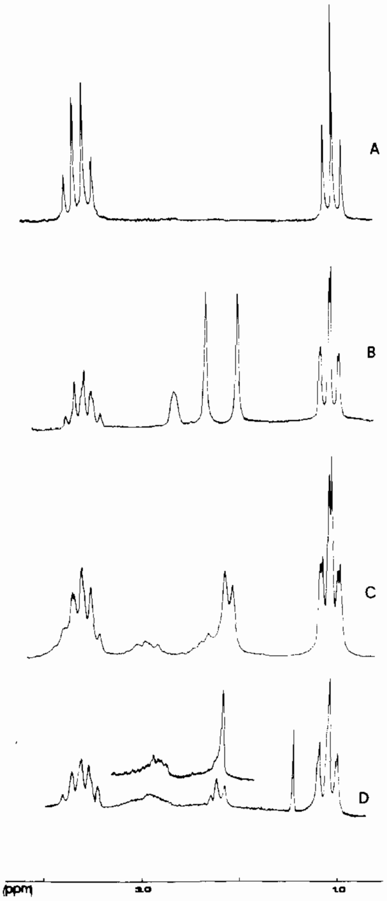


Fig. 1. The Pmr spectra of: (A) Co(Et$_2$dtc)$_3$; (B) [Co(Et$_2$dtc)$_2$Me$_2$enMe$_2$]BF$_4$; (C) [Co(Et$_2$dtc)$_2$HMeenMeH]BF$_4$; (D) [Co(Et$_2$dtc)$_2$HMeenH$_2$]BF$_4$ in CDCl$_3$ solutions and the N-methyl portion of the spectrum after amine proton deuteration.

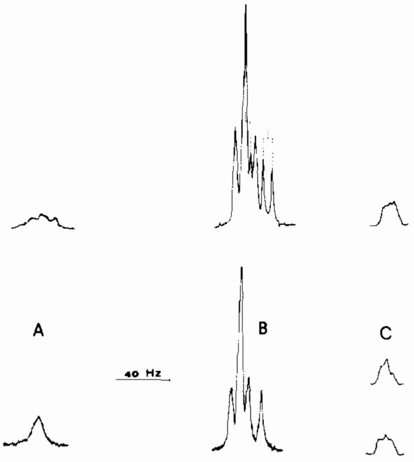
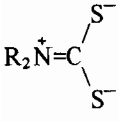


Fig. 2. Double resonance Pmr experiments: the single resonance (top) and the double resonance spectra (bottom) of: A) the methylenic signal at 2.92 ppm of HMeenMeH derivative when irradiating the methylenic resonance at 2.44 ppm (see Fig. 1C); B) the methyl signal of HisoPrenH$_2$ when irradiating the CH resonance at 3.28 ppm; C) the methylenic signal at 2.69 ppm of Me$_2$enMe$_2$ (see Fig. 3), when irradiating the N-methyl resonances at 2.45 and 2.14 ppm.

Infrared Spectra

I.r. spectra of M(dtc)$_3$ complexes have been extensively studied and it is well established that the band in the 1450–1550 cm^{-1} region is attributed to the stretching vibration of the C$\overset{\cdots}{-}$N band. In our complexes this band falls at (1515 ± 5) vs cm^{-1}, about 20 cm^{-1} higher than in Co(Et$_2$dtc)$_3$ (ν(CN) = 1498 cm^{-1}) in CH$_2$Cl$_2$ solutions. This indicates that the resonance form



$$R_2\overset{+}{N}{=}C(S^-)_2$$

gives a higher contribution to the total structure in agreement with the higher charge on the metal atom with respect to the trisdithiocarbamates. This fact is attributed to the presence of one chelating neutral ligand.

The band related to ν(C=S) vibration falls at 1005 cm^{-1} in the Co(Et$_2$dtc)$_3$ derivative, and the presence of only one absorption in the 1050–950 cm^{-1} region is indicative of symmetrically bound dtc group [9]. We observed a band at (995 ± 5) m cm^{-1}, but unfortunately it falls near the broad band centered at 1070 cm^{-1} characteristic (together with the 533–525 cm^{-1} doublet) of the BF$_4$ group, making this band relatively insignificant. The (357 ± 7) ms cm^{-1} band is associated with Co–S vibrations. The ν(NH) bands of ethylenediamines are shifted by about 50 cm^{-1} to lower frequencies on going from the free ligand to the complexes, indicating that the N atom is involved in the coordination [7]. Frequencies in these derivatives are in the ranges 3270–3330 s and 3250–3280 s cm^{-1} (CH$_2$Cl$_2$ solutions). The ν(Co–N) vibration was not observed, but the intensity of this band is reported to be frequently very weak [8].

Electronic Absorption Spectra

The spectra of the complexes are summarized in Table II. In mixed-ligand six-coordinate Co(III) derivatives of lower symmetry than O$_h$, a splitting of one or both the allowed ligand field bands in O$_h$ symmetry is expected.

Unfortunately, the dithiocarbamato Co(III) derivatives [10] give rise to metal-to-ligand and ligand-to-metal charge-transfer transitions in the region ranging from 32 kK to the region containing d–d transitions, often obscuring these bands (as in the above derivatives). Therefore it was impossible to obtain information about the differences in the field strengths of the various ligands from the splitting

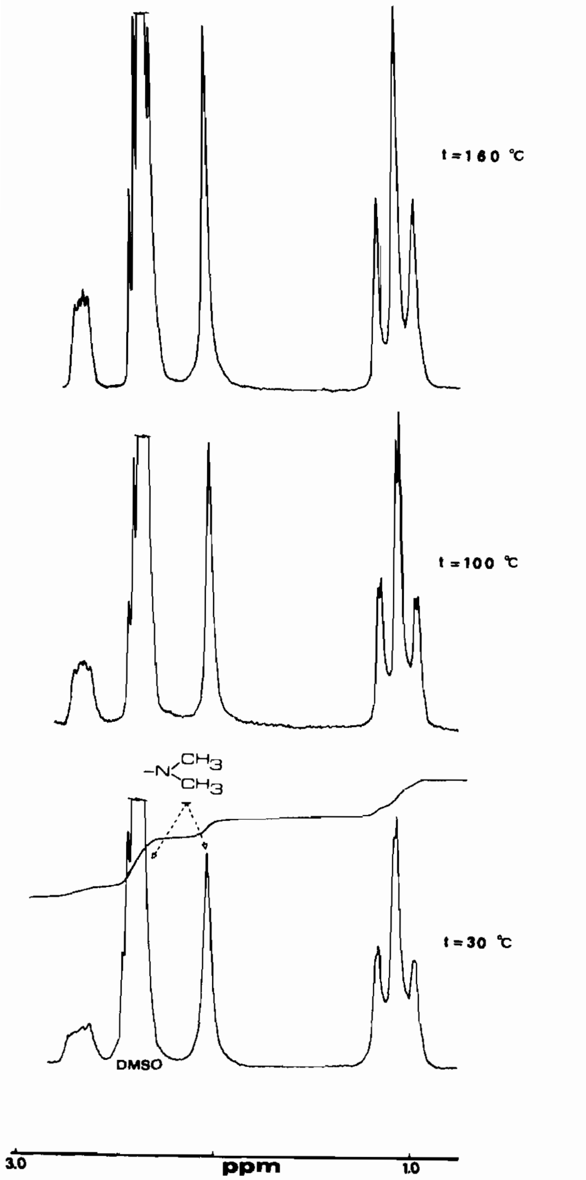


Fig. 3. Temperature dependence of Me_2enMe_2 derivative. Pmr spectra in DMSO-d_6.

of the absorption bands [11]. Only the band near 17 kK may be unambiguously attributed to a d–d electronic transition. On the basis of O_h microsymmetry rather than the actual symmetry of each complex ion, this band may be assigned to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition [12]. The position of this band is shifted to lower energies as the hydrogens on the nitrogen atoms of H_2enH_2 are progressively substituted by alkyl groups. As observed earlier this shift is probably due to the lengthening of metal–ligand bonds to accomodate N-substituted alkyl groups [13].

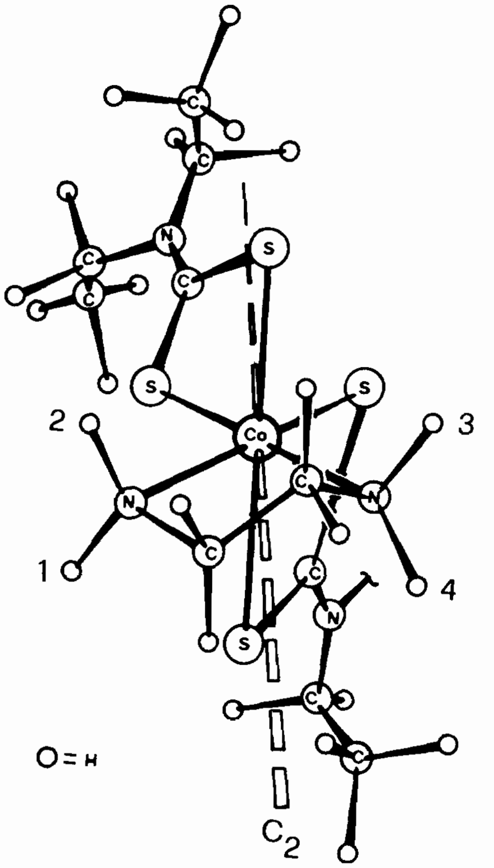


Fig. 4. Proposed structure of the H_2enH_2 derivative.

Pmr Spectra

A complete resonance attribution for all the investigated complexes was performed with the aid of double resonance experiments as well as of spectral analysis on the deuterated samples, as reported for some cases in Figs. 1 and 2. Table III summarizes the proposed assignments. The p.m.r. spectra of the Me_2enMe_2, HMeenMeH, and $HMeenH_2$ derivatives are reported in Fig. 1 and discussed below as typical examples of tetra-di- and mono-substituted ethylenediamine derivatives.

The Me_2enMe_2 derivative

In the spectrum of Me_2enMe_2 complex (Fig. 1B) at least two main sets of quartets and triplets with J = 7 Hz due to the ethyl groups of the dtc ligand can be identified. This resonance pattern can be attributed both to the slow S_2C–NR_2 bond rotation on nmr time scale [14], and to the existence of a two-fold axis passing in the middle point of the CH_2–CH_2 bond of the en ligand and through the Co atom (see Fig. 4). Such an axis relates these ethyl groups together on a two by two basis. The corresponding $Co(Et_2dtc)_3$ derivative spectrum instead shows a single sharp triplet and a quartet, as expected for the

O_h symmetry (see Fig. 1A for comparison). The CH_2-CH_2 resonances of the en ligand give a poorly resolved peak which is not affected by a temperature increase (see later). Spectral features of Co(III) ethylenediamine complexes very similar to those obtained in our case are reported in the literature [15]. They are generally attributed to the diamine chelate ring in a gauche conformation according to X-ray results, which have revealed that coordinated ethylenediamines adopt the gauche conformation without exception [16]. These protons of the en ring should then behave as an AA′BB′ spin system. The unresolved broad band was generally explained [15] admitting that:

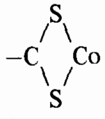
i) if the inversion of the conformation is slow, the chemical shift difference between the axial and equatorial protons must be very small, giving an envelope of a complex system of multiplets;

ii) if the ring inversion is rapid on the nmr scale, the broad band can be attributed to the effective chemical shift difference between the axial and equatorial protons, together with the effective coupling constants between them.

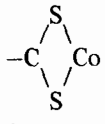
iii) a coupling of the protons with the Cobalt nucleus is present.

In our case this band is not significantly sharpened by the temperature increase (see Fig. 3), therefore hypotheses ii) and iii) seem more likely. Our experiments are evidence of a further source of this apparent broadening due to a long range coupling of CH_3 protons of the N substituents with the protons of the CH_2-CH_2 system. In fact, the irradiation of the CH_3 resonances (see Fig. 2C) strongly affects the pattern of this band.

More significant, in view of assigning the stereochemical structure of the complex, are the $N-CH_3$ resonances. The two 1:1 well separated signals are diagnostic of two different magnetic environments for the CH_3 groups. For symmetry reasons (refer to Fig. 4) the protons of a CH_3 put in position 1 or 2 are equivalent to those put in position 3 or 4 respectively, and the two pairs will never become equivalent whether the ring inversion is rapid or slow. In fact, the CH_3 (2,4) protons are located above the plane identified by the



fragment, while the CH_3 (1,3) protons always lie away from the chelate ring. The



fragment, due to the presence of π delocalized electrons, is expected to produce magnetic anisotropy in such a way that the methyl 1 and 3 protons, lying away from the plane of the chelating ring, will be de-shielded, while the methyl 2 and 4 protons, located above this plane, will be shielded. These facts clearly explain the remarkable chemical shift difference between the CH_3 peaks, that do not coalesce even at 160 °C in DMSO, showing the inertness of the coordinated nitrogen atom towards the inversion of configuration. The coalescence of CH_3 and CH_2 signals of dithiocarbamato ligand is due to the S_2C-N bond rotation.

On this basis the molecular model of Fig. 4 is consistent with the nmr data. The expected presence of the optical isomers (Λ and Δ), due to the asymmetric Co centre, are obviously undetectable by our nmr experiments.

The HMeenMeH derivative

The spectrum of the HMeenMeH derivative (Fig. 1C) exhibits resonances of ethyl groups similar to those of the Me_2enMe_2 complex. The N-methyl protons exhibit a broadened doublet, which collapses to a singlet and becomes sharper in the N-deuterated form. Hydrogen isotope exchange was obtained using NaOD, no deuteration occurring in D_2O and/or DCl.

The $N-CH_3$ signals are not sharp because: i) they are coupled with the CH_2-CH_2 protons and ii) they overlap partially with the NH resonances, as confirmed by a spectrum carried out at 360 MHz. The chemical shift of this CH_3 group lies close to the value of the more shielded CH_3 groups on the Me_2enMe_2 derivative. On these bases for this complex we suggest the conformation as having the methyl groups in position 2 and 4.

When coordinated, N–N′ symmetrically substituted diamines can exist in (R,R), (S,S) or (R,S) forms, where R and S are referred to the chirality of the coordinated nitrogen centre [17]. The CH_3 groups in the 2 and 4 positions give ethylenediamine the (R,R) form in the Fig. 4, where the complex is drawn as Δ enantiomer (chirality of the Co centre), and we may thus conclude that the only isomers obtained are the Δ(R,R) and the enantiomer Λ(S,S), for which an identical nmr spectrum is expected.

These results are in agreement with those previously reported for other HMeenMeH derivatives of Co(III) [17]. The methylene resonances of en consist of two well separated enveloped bands, due to two pairs of protons affected by the presence of only one Me orientation.

The broadening of each resonance can be explained in the same way as the results obtained for the Me_2enMe_2 derivative.

The HMeenH$_2$ derivative

The $HMeenH_2$ complex shows the CH_3 resonances of Fig. 1D with similar features as the HMeenMeH complex. Therefore we assign this complex the same stereochemistry of the Fig. 4 with the N-methyl group in the 2 or 4 position, and for the Λ enantiomer in the 1 or 3 position.

The asymmetry of the $HMeenH_2$ ligand is reflected in the asymmetry of the signals related to the Et groups of the dtc ligands and to CH_2-CH_2 of en.

The remaining derivatives HEtenEtH, $HEtenH_2$, $HPrenH_2$ and $HisoPrenH_2$ follow the same nmr behaviour discussed above for the di- and mono-N-substituted derivatives respectively.

The two CH_3 groups of $HisoPrenH_2$ derivative are diastereotopic due to the chiral centre at the nitrogen atom, and exhibit two distinct doublet signals that do not coalesce even at 160 °C. This last fact indicates again the inertness of the coordinated N atom towards the inversion of configuration.

On these bases, if the signals of the possible diastereoisomers are not accidentally the same, we point out a strong stereoselectivity in the preparation of these derivatives, when the coordinated N-substituted diamines have chiral centres at one or both the nitrogen atoms. The nature of this stereoselectivity is not clear.

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