Photochemical Synthesis and Crystal Structures of Tetrakis(ethane-1,2-diamine)dicobalt(III) Complexes bridged by 1,3,5-Triazine-2,4,6-trithionate and 4-Oxo-1,3,5-triazine-2,6-dithionate†

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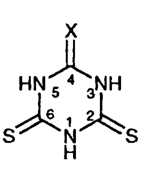
Two kinds of dinuclear cobalt(III) complexes *sym*-(*meso*- and *rac*-)$[\{Co(en)_2\}_2(\mu\text{-ttcy})]X_3$ and *sym*-[*meso*- and *rac*-)$[\{Co(en)_2\}_2(\mu\text{-dtcy})]X_3$ (en = ethane-1,2-diamine, H_3ttcy = 1,3,5-triazine-2,4,6-trithione, H_3dtcy = 4-oxo-1,3,5-triazine-2,6-dithione) have been prepared photochemically from $[Co(en)_3]Cl_3$, H_3ttcy and NaOH and characterized by elemental analysis, IR, UV/VIS and NMR spectroscopy. The dtcy complexes are formed *via* a novel desulfurization of the ttcy ligand. Two crystal structures, *sym-meso*-$[\{Co(en)_2\}_2(\mu\text{-ttcy})][ClO_4]_3\cdot 2H_2O$ and *sym-meso*-$[\{Co(en)_2\}_2(\mu\text{-dtcy})]I_3\cdot 4H_2O$ were determined from 1859 and 4146 reflections to $R = 0.056$ ($R' = 0.060$) and $R = 0.069$ ($R' = 0.073$), respectively: monoclinic, space group $P2_1/a$, $a = 14.392(4)$, $b = 14.807(4)$, $c = 14.816(4)$ Å, $\beta = 92.83(3)°$ and $Z = 4$; monoclinic, space group $P2/c$, $a = 18.088(3)$, $b = 8.146(6)$, $c = 21.757(3)$ Å, $\beta = 93.25(1)°$ and $Z = 4$. The bridging ttcy and dtcy ligands co-ordinate symmetrically through the two N and S donor sets and both complexes are in the *meso* form. Marked symmetric intramolecular hydrogen bonds N–H···S[N···S 3.19(1), 3.21(1) Å] were formed between the free sulfur atom of the ttcy and the two amine protons of the en in the ttcy complex.

The co-ordination chemistry of heterocyclic thione donors is of interest both from a biological and pharmaceutical perspective and these compounds have a wide range of applications.[1] Recently we reported the photochemical synthesis and characterization of some cobalt(III) complexes containing pyridine-2-thione (Hpyt),[2] pyrimidine-2-thione (Hpymt) and its derivatives,[3] 2-thiouracil (H_2tuc) and its related ligands[4] and 2,4-dithiouracil (H_2dtuc).[5] In the tuc and dtuc complexes, an intramolecular hydrogen bond plays an important role in stabilizing a sterically unfavourable linkage isomer.

1,3,5-Triazine-2,4,6-trithione [trithiocyanuric acid (H_3ttcy)] has three N,S-donor sets and more diverse donor behaviours are expected as compared with the above ligands. Chudy and Dalziel[6] have reported some polynuclear complexes of Cu^{II}, Cd^{II}, Hg^{II}, Pb^{II}, Pd^{II}, Ag^{I} and Bi^{III}. Cobin *et al.*[7] reported a trinuclear titanium(III) complex. However, these complexes are in general amorphous and insoluble powders and their characterization is still insufficient.

In order to clarify the donor properties of the ttcy ligand, we attempted the photochemical preparation of the dinuclear ttcy–cobalt(III) complexes $[\{Co(en)_2\}_2(\mu\text{-ttcy})]^{3+}$ (en = ethane-1,2-diamine). In this preparation, the concomitant formation of a second type of dinuclear complex with 4-oxo-1,3,5-triazine-2,6-dithionate (H_3dtcy = dithiocyanuric acid) $[\{Co(en)_2\}_2(\mu\text{-dtcy})]^{3+}$ was also observed. The latter is formed *via* a novel desulfurization reaction of ttcy. These complexes were characterized by elemental analysis, UV/VIS absorption, infrared, ^1H and ^{13}C NMR spectra and X-ray crystal structure analysis.



X = S H_3ttcy
X = O H_3dtcy

Experimental

Preparation of the Complexes.—The compound H_3ttcy (0.71 g, Aldrich) was suspended in warm water (200 cm^3) and the pH was adjusted to 8–9 by adding aqueous NaOH solution. To the mixture was added *rac*-$[Co(en)_3]Cl_3$ (3.2 g) and a yellow precipitate, probably the trithiocyanurate salt of $[Co(en)_3]^{3+}$, appeared soon. The suspension was divided into eight quartz reaction tubes (30 cm^3) and nitrogen gas was bubbled through the suspensions for 20 min. Irradiation with a Toshiba 500 W halogen lamp in the absence of a filter was carried out for 3 h. The yellow precipitate disappeared in 2.5 h and insoluble dark red fine crystals, of composition $[Co(ttcy)(en)_2]$ (**5**, yield 40%), were formed and filtered off. The filtrate was left to stand at room temperature for 2 d to give a small amount of dark precipitate. After filtration, the filtrate was poured onto a column of cation exchanger (SP-Sephadex C-25, Na^+ form, 3.5 × 120 cm). Elution with 0.3 mol dm^{-3} Na_2SO_4 gave three coloured bands, red, red and yellow, in this order. The last yellow complex was the starting material $[Co(en)_3]^{3+}$. Circular dichroism (CD) spectral measurements of the fractions confirmed that each red band is composed of two species: the first contains the species **1** and **2** and the second band **3** and **4**. The leading and trailing parts of the column fractions of species **2** or **3** showed enantiomeric CD spectra, which means they are racemic. The other species **1** and **4** however showed no CD activity. The overall yield was 33% for the first band and 15% for the second. Each species was concentrated by rotary

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

evaporation and the white precipitate of Na_2SO_4 obtained upon addition of MeOH was filtered off. After repeated removal of most of the Na_2SO_4 the complexes were crystallized as the iodide (**1**–**3**) or the perchlorate salts (**4**) by using a anion exchange column (QAE-Sephadex A-25). Yields obtained were 4000 mg for **1**, 350 mg for **2**, 180 mg for **3** and 150 mg for **4**.

Complex **1** (Found: C, 13.55; H, 4.25; N, 15.60. Calc. for $[\{Co(en)_2\}_2(\mu\text{-dtcy})]I_3\cdot4H_2O$, $C_{11}H_{40}Co_2I_3N_{11}O_5S_2$: C, 13.65; H, 4.15; N, 15.90%): UV/VIS (water) λ_{max}/nm 506 (ε 301), 360(sh), 317 (25 500), 269 (21 500) and 229 (65 600 $dm^3\ mol^{-1}\ cm^{-1}$). Complex **2** (Found: C, 13.80; H, 4.05; N, 16.05. Calc. for $[\{Co(en)_2\}_2(\mu\text{-dtcy})]I_3\cdot3.5\ H_2O$, $C_{11}H_{39}Co_2I_3N_{11}O_{4.5}S_2$: C, 13.75; H, 4.10; N, 16.05%): UV/VIS (water) λ_{max}/nm 502 (ε 306), 360(sh), 314 (26 400), 266 (22 300) and 227 (73 300 $dm^3\ mol^{-1}\ cm^{-1}$). Complex **3** (Found: C, 13.70; H, 3.85; N, 15.95. Calc. for $[Co(en)_2\}_2(\mu\text{-ttcy})]I_3\cdot2.5H_2O$, $C_{11}H_{37}Co_2I_3N_{11}O_{2.5}S_3$: C, 13.80; H, 3.90; N, 16.10%): UV/VIS (water) λ_{max}/nm 511 (ε 261), 360(sh), 317 (21 600), 270(sh) (25 500) and 227 (75 000 $dm^3\ mol^{-1}\ cm^{-1}$). Complex **4** (Found: C, 15.65; H, 4.25; N, 17.65. Calc. for $[\{Co(en)_2\}_2(\mu\text{-ttcy})][ClO_4]_3\cdot2H_2O$, $C_{11}H_{36}Cl_3Co_2N_{11}O_{14}S_3$: C, 15.25; H, 4.20; N, 17.75%): UV/VIS (water) λ_{max}/nm 513 (ε 279), 360(sh), 319 (22 100), 270(sh) (26 800), 243 (47 700) and 210(sh) (30 300 $dm^3\ mol^{-1}\ cm^{-1}$).

The insoluble dark red crystals **5** had composition $[Co(ttcy)(en)_2]$ and were converted quantitatively in 40% $HClO_4$ solution to the water-soluble perchlorate salt $[Co(H_2ttcy)(en)_2][ClO_4]_2$ **6**. Complex **5** (Found: C, 22.65; H, 5.00; N, 26.05. Calc. for $[Co(ttcy)(en)_2]\cdot H_2O$, $C_7H_{18}CoN_7OS_3$: C, 22.65; H, 4.90; N, 26.40%). Complex **6** (Found: C, 14.25; H, 3.60; N, 16.50. Calc. for $[Co(H_2ttcy)(en)_2][ClO_4]_2\cdot2H_2O$, $C_7H_{22}Cl_2CoN_7O_{10}S_3$: C, 14.25; H, 3.75; N, 16.60%): UV/VIS (0.01 mol dm^{-3} HCl) λ_{max}/nm 512.5 (ε 185), 360(sh), 319 (15 100), 270(sh) (18 000), 243 (32 300) and 210(sh) (21 000 $dm^3\ mol^{-1}\ cm^{-1}$).

X-Ray Crystal Structure Determination of sym-$[\{Co(en)_2\}_2(\mu\text{-dtcy})]I_3\cdot4H_2O$ **1** *and sym*-$[\{Co(en)_2\}_2(\mu\text{-ttcy})][ClO_4]_3\cdot2H_2O$ **4**.—*Crystal data of* **1**: $C_{11}H_{40}Co_2I_3N_{11}O_5S_2$, M = 969.22, monoclinic, space group $P2/c$ (no. 13), a = 18.088(3), b = 8.146(6), c = 21.757(3) Å, β = 93.25(2)°, U = 3201(3) $Å^3$, Z = 4, D_c = 2.012 g cm^{-3}, $F(000)$ = 1872, red crystal, 0.15 × 0.15 × 0.30 mm and μ(Mo-Kα) = 40.6 cm^{-1}.

Crystal data of **4**: $C_{11}H_{36}Cl_3Co_2N_{11}O_{14}S_3$, M = 866.89, monoclinic, space group $P2_1/a$ (no. 14), a = 14.392(4), b = 14.807(4), c = 14.816(4) Å, β = 92.83(3)°, U = 3153(3) $Å^3$, Z = 4, D_c = 1.827 g cm^{-3}, $F(000)$ = 1776, red crystal, 0.05 × 0.20 × 0.30 mm and μ(Mo–Kα) = 15.7 cm^{-1}.

Data collection and processing. For crystal **1**, Rigaku AFC5 diffractometer, ω–2θ mode with ω-scan width = 1.05 + 0.35 tan θ, scan speed 6° min^{-1}, graphite-monochromated Mo–Kα radiation; 6450 reflections measured (2.0 < θ < 27.5°), after absorption corrections (maximum, minimum transmission factors = 1.00, 0.77), giving 4146 reflections with $F_o > 3\sigma(F_o)$. For crystal **4**, 3327 reflections measured (2.0 < θ < 25.0°), after absorption correction (maximum, minimum transmission factors = 1.00, 0.75), giving 1859 reflections with $F_o > 3\sigma(F_o)$.

Structure analysis and refinement. For crystal **1**, direct methods followed by normal heavy-atom procedures. The final cycle of block-diagonal matrix least-squares refinement was based on 4146 observed reflections and 307 variable parameters. The final values of R and R' were 0.069 and 0.073, respectively. For crystal **4**, based on 1859 observed reflections and 397 variable parameters, the final values of R and R' were 0.056 and 0.060, respectively. Large thermal parameters probably related to positional disorder were found for several oxygen atoms of the perchlorate anion [O(5)–O(8)]. The highest peak (1.5 e $Å^{-3}$) in the final electron density difference map of complex **4** is found at 0.025, 0.305, 0.575 but the hydrogen atoms of the water molecules could not be located. All calculations were performed using the UNICS III software package[8] on a HITAC M680 Hitachi computer at the Computer Center of the Institute for Molecular Science, Okazaki.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Measurements.—The UV/VIS absorption spectra were recorded with a Hitachi 330 spectrophotometer, CD spectra with a JASCO J-500 spectropolarimeter and ^1H and ^{13}C NMR spectra with a JEOL JNM-GSX-400 spectrometer in D_2O or $(CD_3)_2SO$. X-Ray crystal structure analysis was made at the Institute for Molecular Science.

Results and Discussion

Characterization of the Complexes.—In the column chromatography, two red bands were found. Complexes **1** and **2** were isolated from the first band and complexes **3** and **4** from the second. Complexes **1** and **2** show similar UV/VIS absorption spectra (see Experimental section). The first d–d absorption band appears at 502–506 nm and the intense sulfur-to-metal charge-transfer (c.t) band at 314–317 nm (ε = *ca*. 26 000 $dm^3\ mol^{-1}\ cm^{-1}$). The absorption spectra of complexes **3** and **4** are also similar to each other but are slightly different from those of **1** and **2**. The first d–d bands of complexes **3** and **4** are red-shifted (511 for **3** and 513 nm for **4**) relative to **1** and **2** and the intensities of the c.t. bands are slightly reduced as shown in Fig. 1. All the spectra are characteristic of thionato complexes of a CoN_5S type such as $[Co(pyt)(en)_2]^{2+}$,[2] $[Co(pymt)(en)_2]^{2+}$[3] and $[Co(tuc)(en)_2]^+$,[4] and so are concluded to have this chromophore.

The elution behaviour of the above complexes resembles that of $[Co(en)_3]^{3+}$ and all complexes appear to have +3 ionic charge. Since the ttcy ligand has three N,S-donor sets, the formation of polynuclear complexes are expected. Two dinuclear complexes (symmetrical and unsymmetrical isomers **a** and **b**) and a trinuclear complex **c** can be considered. In each there are further optical isomers based on the configuration (Δ or Λ) of the skew pairs of the chelate rings about the cobalt(III) ion:[9] one *meso* and one racemic (*rac*) form for **a**, two *rac* forms for **b** and two *rac* forms for **c**. Carbon-13 NMR spectroscopy is useful to differentiate between these isomers: two signals are expected for **a**, three for **b** and one for **c** in the ttcy chemical shift region. The NMR data are shown in Table 1. Complexes **1** and **2** showed two signals at δ 188.50 and 159.83 and at δ 188.91 and 160.55, respectively, although the value at δ *ca*. 160 occurs at too high a magnetic field to be assigned as arising from C=S.

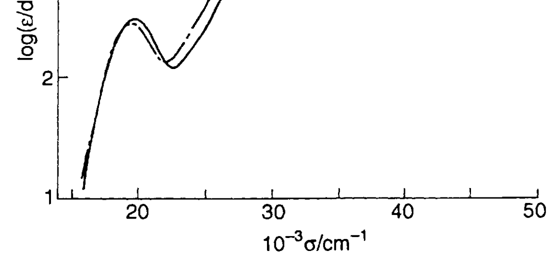
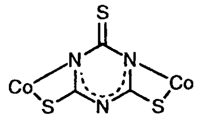


Fig. 1 UV/VIS absorption spectra of complex **1** (——) and complex **4** (— — —)

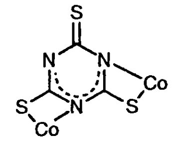
Table 1 Carbon-13 NMR spectral data (δ)*

Complex	Solvent	$\delta(^{13}C)$
1	$(CD_3)_2SO$	188.50 (C^2 and C^6), 159.83 (C^4) 47.04, 46.16, 46.02, 45.20 (en)
2	$(CD_3)_2SO$	188.91 (C^2 and C^6), 160.55 (C^4) 45.64, 44.94, 44.87, 44.03 (en)
3	D_2O	190.16 (C^4), 187.22 (C^2 and C^6) 47.27, 46.08, 45.77, 44.66 (en)
4	D_2O	190.32 (C^4), 187.20 (C^2 and C^6) 47.27, 46.08, 45.77, 44.66 (en)
	$(CD_3)_2SO$	188.49 (C^4), 185.91 (C^2 and C^6) 46.14, 45.31, 44.96, 43.67 (en)
6	$(CD_3)_2SO$	180.46, 179.90 (C^2 and C^4), 172.03 (C^6), 45.98, 45.29, 45.17, 44.57 (en)

* Downfield relative to $SiMe_4$ in $(CD_3)_2SO$ and dioxane (δ 67.40) in D_2O.



a



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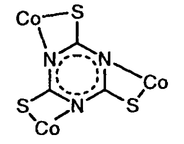

c

Complexes 3 and 4 gave also two signals at δ 190.16 and 187.22 and at δ 190.32 and 187.20, respectively, in the same region. Based on the above symmetry argument all complexes have the symmetrical dinuclear structure **a**. The ^{13}C chemical shifts and UV/VIS absorption spectra of **1** and **2** or **3** and **4** are similar to each other, respectively. It is thus reasonable to consider that they are *meso* and *rac* optical isomers. In the SP-Sephadex C-25 column separation with 0.25 mol dm^{-3} Na_2SO_4,[10] the leading and trailing fractions of complex **2** showed (−) and (+) CD bands respectively in the first d–d band.* Complex **3** also showed similar enantiomeric CD spectra but the fractions of **1** and **4** showed no CD activity. Therefore, complexes **1** and **2** are the *meso*- and *rac*-isomers of one symmetrical dinuclear complex and complexes **3** and **4** are *rac*- and *meso*-isomers of a second symmetrical dinuclear complex, respectively.

Infrared spectra gave an important clue for the characterization of the complexes. Fig. 2 shows the infrared spectra of the present and related complexes in the region 1500–1700 cm^{-1}. These complexes are structurally analogous and have the pyrimidine-2-thionato skeleton in common. The complexes $[Co(pymt)(en)_2]^{2+}$ and $[Co(dtuc)(en)_2]^+$ which have no oxygen atom on the pyrimidine ring exhibited one or two absorptions due to the thioamide band I^1 and/or δ(NH) in the region 1500–1600 cm^{-1} but no absorptions > 1600 cm^{-1}. On the other hand, $[Co(tuc)(en)_2]^+$ and $[Co(tbba)(en)_2]^+$ [tbba = 2-thiobarbiturate(2−), 2-thioxopyrimidine-4,6-dionate][11] which have one or two oxygen atoms as pyrimidine ring substituents showed additional absorptions in the region 1620–1640 cm^{-1} due to the ν(C=O) vibration.[12] Therefore the presence of a band > 1600 cm^{-1} is diagnostic of C=O. In the infrared spectra of **1** and **4**, only complex **1** gave such a band (at 1630 cm^{-1}) indicating that while complex **4** contains ttcy, complex **1** does not. The bridging ligand in complex **1** closely resembles ttcy but contains a C=O group. The high field chemical shift of one of the ^{13}C NMR signals, δ 159.83 in **1** and 160.55 in **2**, also suggests the presence of the C=O group. 4-Oxo-1,3,5-triazine-2,6-dithionate satisfies the above requisites. Thus, complexes **1** and **2** are assigned as *sym*-$[\{Co(en)_2\}_2(\mu\text{-dtcy})]^{3+}$ and complexes **3** and **4** as *sym*-$[\{Co(en)_2\}_2(\mu\text{-ttcy})]^{3+}$. Elemental analyses are in good agreement with these formulations (see Experimental section).

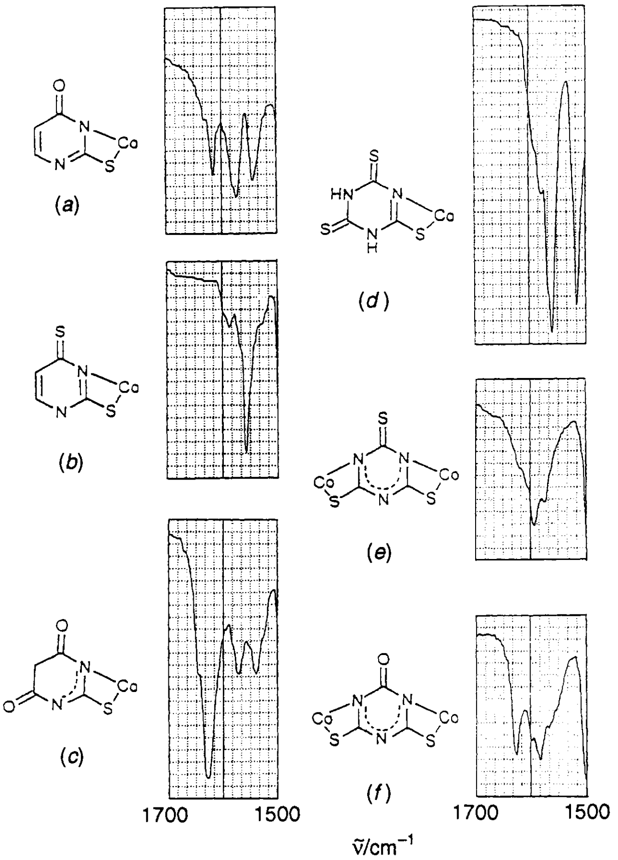

Fig. 2 Comparison of infrared spectra in the related complexes with a pyrimidine-2-thionato skeleton: (*a*) $[Co(tuc)(en)_2]ClO_4{\cdot}H_2O$, (*b*) $[Co(dtuc)(en)_2]ClO_4$, (*c*) $[Co(tbba)(en)_2]ClO_4$, (*d*) complex **6**, (*e*) complex **4** and (*f*) complex **1**

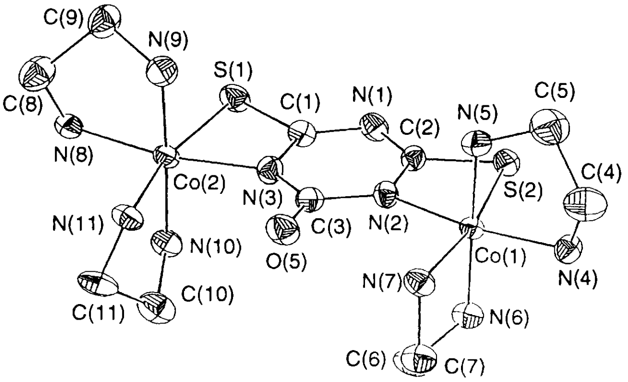

Fig. 3 An ORTEP drawing of *sym-meso*-$[\{Co(en)_2\}_2(\mu\text{-dtcy})]I_3{\cdot}4H_2O$ **1** with thermal ellipsoids drawn at the 50% probability level

Crystal Structure of sym-$[\{Co(en)_2\}_2(\mu\text{-dtcy})]I_3{\cdot}4H_2O$ **1**.—Fig. 3 shows the ORTEP[13] drawing of complex **1** and the atomic parameters are listed in Table 2. The bond distances and angles obtained by the average of chemically equivalent bonds are shown in Fig. 4(*a*) together with those of related complexes [Fig. 4(*b*) and 4(*d*)]. Individual bond lengths and angles about the cobalt centres are summarized in Table 3. For the discussion below, the data of Fig. 4(*a*) are used.

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* The achievement of partial optical resolution using Na_2SO_4 is rare but not unprecedented because SP-Sephadex resins are composed of chiral D-glucose. The elution order is often reversed compared to that with chiral elution agents such as $Na_2[Sb_2(D\text{-}H_2tart)_2]$ and $Na_2(D\text{-}H_2tart)$ (H_4tart = tartaric acid).

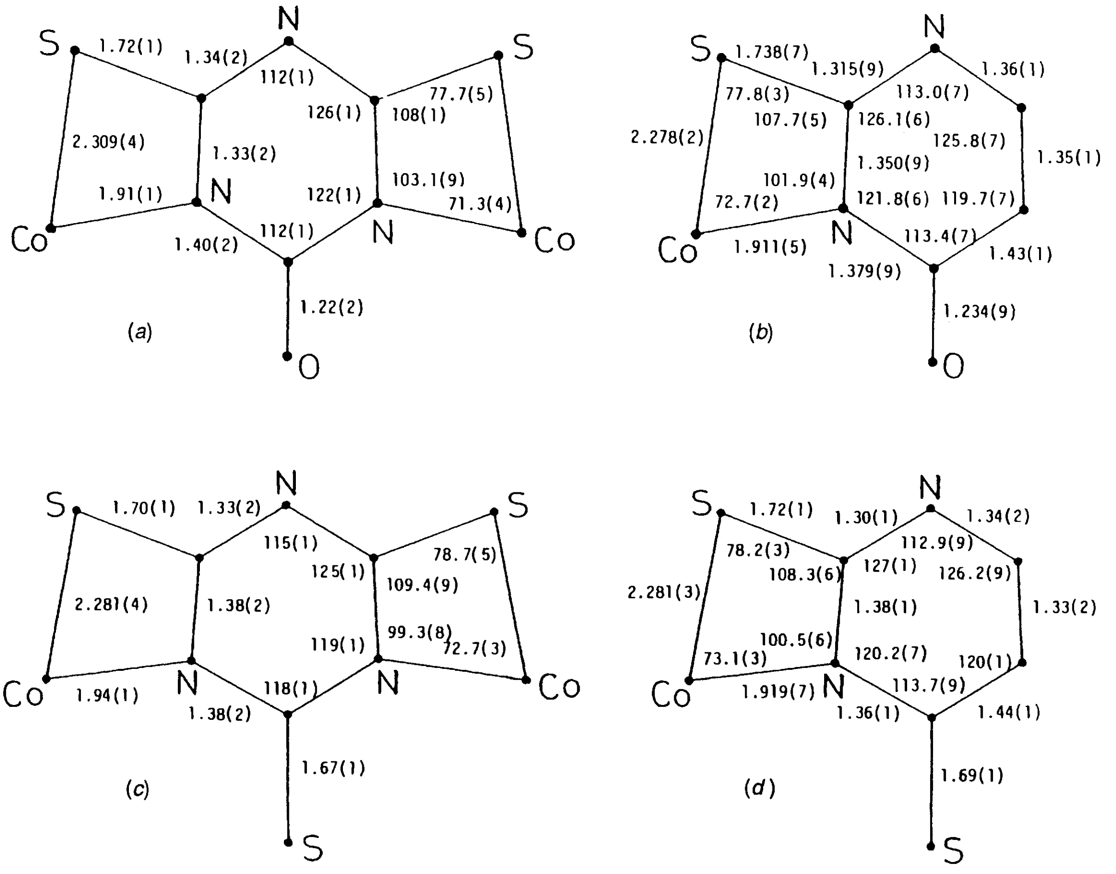

Fig. 4 Comparison of bond lengths (Å) and angles (°) in related complexes containing four-membered chelate systems: (*a*) *sym-meso*-[{Co(en)$_2$}$_2$(μ-dtcy)]I$_3$·4H$_2$O **1**, (*b*) [Co(tuc)(en)$_2$]ClO$_4$, (*c*) *sym-meso*-[{Co(en)$_2$}$_2$(μ-ttcy)][ClO$_4$]$_3$·2H$_2$O **4** and (*d*) [Co(dtuc)(en)$_2$]ClO$_4$

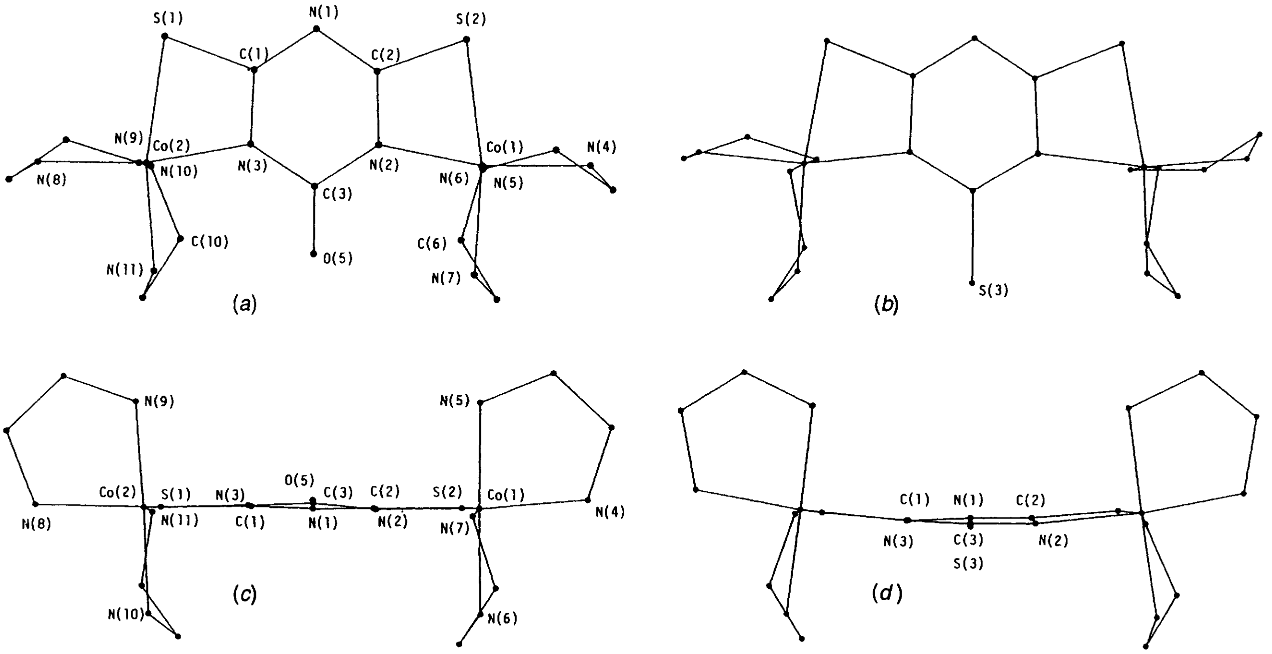

Fig. 5 Projected top- [(*a*) complex **1**, (*b*) complex **4**] and side-views [(*c*) complex **1**, (*d*) complex **4**]. The numbering scheme of complex **4** is the same as that of complex **1** except for S(3) instead of O(5).

The bridging dtcy ligand is quadridentate using two symmetric N,S-donor sets. The bond length between the C atom (with non-co-ordinated substituent) and its substituent atom is 1.22(2) Å which corresponds to a normal C=O bond length and not to a C=S bond. As expected from the infrared spectra, the formation of the dtcy ligand *via* the novel desulfurization reaction from the ttcy ligand is thus confirmed by the X-ray crystal structure analysis.

In the dtcy ligand, four C–N bonds are shorter than the other two C–N bonds which are adjacent to the C=O group: the averages of the former and the latter being 1.34(2) and 1.40(2) Å, respectively. Thus, the dtcy ligand has a delocalized electronic

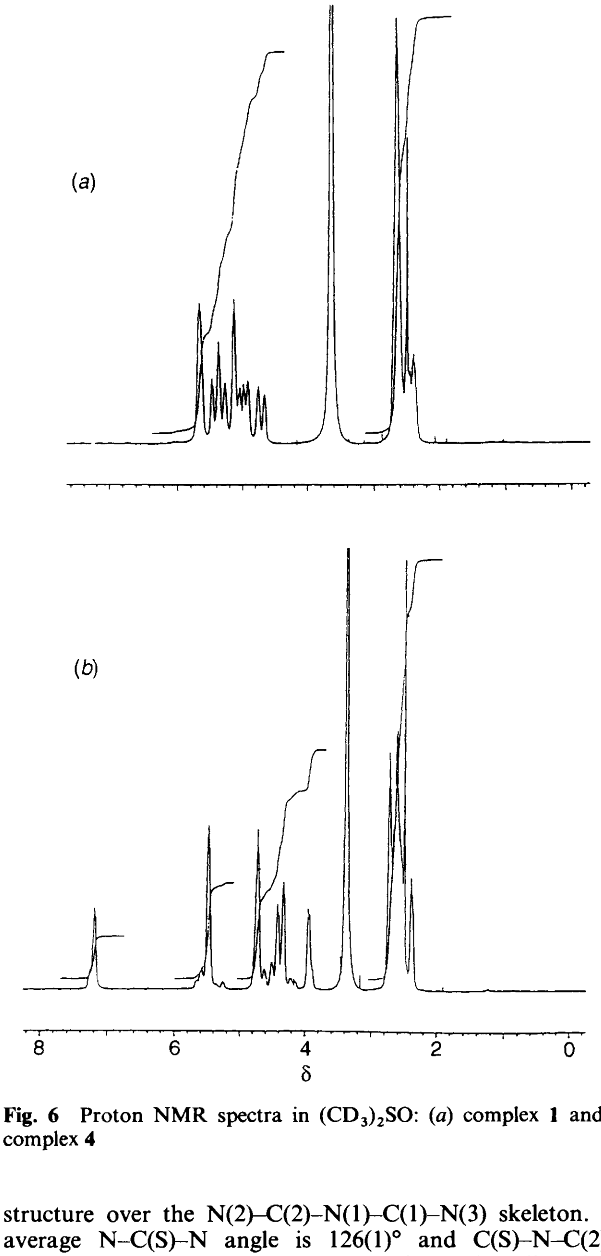

Fig. 6 Proton NMR spectra in $(CD_3)_2SO$: (*a*) complex **1** and (*b*) complex **4**

Table 2 Positional parameters (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
I(1)	1 356(1)	2 025(1)	7 887(1)
I(2)	1 723(1)	−2 546(2)	9 510(1)
I(3)	4 389(1)	7 419(1)	6 367(1)
Co(1)	1 667(1)	1 707(2)	11 226(1)
Co(2)	3 675(1)	1 284(2)	9 082(1)
S(1)	4 119(2)	−987(4)	9 616(2)
S(2)	2 320(2)	−612(4)	11 542(2)
O(1)	411(7)	4 460(16)	8 946(6)
O(2)	47(7)	2 746(14)	9 999(6)
O(3)	5 707(5)	−6 903(13)	8 794(5)
O(4)	1 894(7)	3 755(16)	2 937(5)
O(5)	2 226(5)	3 033(12)	9 816(5)
N(1)	3 262(6)	−941(13)	10 619(5)
N(2)	2 385(6)	1 227(14)	10 639(5)
N(3)	3 126(6)	1 025(13)	9 802(5)
N(4)	968(6)	1 712(14)	11 883(5)
N(5)	915(6)	402(15)	10 769(6)
N(6)	2 391(6)	3 110(14)	11 682(5)
N(7)	1 285(6)	3 787(13)	10 845(5)
N(8)	4 312(6)	1 112(14)	8 379(5)
N(9)	2 992(6)	−98(14)	8 584(6)
N(10)	4 370(6)	2 737(13)	9 553(5)
N(11)	3 184(6)	3 326(14)	8 789(5)
C(1)	3 435(7)	−299(16)	10 075(6)
C(2)	2 709(7)	−122(16)	10 866(6)
C(3)	2 537(7)	1 851(17)	10 063(7)
C(4)	220(8)	1 246(21)	11 636(7)
C(5)	364(8)	−266(20)	11 172(7)
C(6)	2 409(9)	4 810(19)	11 422(7)
C(7)	1 543(9)	5 214(18)	11 217(8)
C(8)	3 892(9)	458(21)	7 820(8)
C(9)	3 351(9)	−922(21)	8 088(8)
C(10)	4 037(8)	4 405(17)	9 597(7)
C(11)	3 643(8)	4 775(18)	8 943(7)

Table 3 Selected bond distances (Å) and bond angles (°) for complexes **1** and **4**

	1	**4**
Co(1)–N(4)	1.962(11)	1.914(12)
Co(1)–N(5)	1.952(12)	1.972(12)
Co(1)–N(6)	1.965(11)	1.960(13)
Co(1)–N(7)	1.992(11)	1.963(12)
Co(2)–N(8)	1.972(11)	1.948(12)
Co(2)–N(9)	1.953(12)	1.951(13)
Co(2)–N(10)	1.971(11)	1.962(12)
Co(2)–N(11)	1.974(11)	1.968(12)
S(2)–Co(1)–N(7)	167.9(4)	170.3(4)
N(2)–Co(1)–N(4)	167.7(5)	167.6(5)
N(5)–Co(1)–N(6)	177.3(5)	177.2(5)
N(4)–Co(1)–N(5)	85.1(5)	86.0(5)
N(6)–Co(1)–N(7)	85.5(5)	85.1(5)
S(1)–Co(2)–N(11)	167.6(4)	172.2(4)
N(3)–Co(2)–N(8)	168.7(5)	166.8(5)
N(9)–Co(2)–N(10)	177.6(5)	177.8(5)
N(8)–Co(2)–N(9)	84.7(5)	86.1(5)
N(10)–Co(2)–N(11)	85.6(5)	85.0(5)

structure over the N(2)–C(2)–N(1)–C(1)–N(3) skeleton. The average N–C(S)–N angle is 126(1)° and C(S)–N–C(2) is 112(1)°. In the six-membered ring of the dtcy ligand, the remaining C–N–C (av.) and the N–C–N angles are 122(1) and 112(1)°, respectively. The large N–C–N angle, 126(1)°, is due to co-ordination of the sulfur to the metal leading to a four-membered chelate ring. The same trend was observed for analogous complexes containing N,S four-membered chelate rings.[3–5]

The absolute configurations about Co(1) and Co(2) are Δ and Λ, respectively, complex **1** being a *meso* optical isomer. The conformation of the four en chelate rings are all oblique (*ob*) to the pseudo-C_3 axis.[14] The *ob* conformation directs one of the NH_2 protons to the intramolecular hydrogen bond with the oxygen of the dtcy, a situation found in many complexes such as $[Co(tuc)(en)_2]^{+}$[4] and $[Co(dtuc)(en)_2]^{+}$.[5] The intramolecular distance N(7) ··· O(5) is 2.95(2) Å [H(N7A) ··· O(5) 2.52(16) Å, N(7)–H(N7A) ··· O(5) 101(12)°] and the distance N(11) ··· O(5) is 2.91(2) Å [H(N11A) ··· O(5) 2.50(16) Å, N(11)–H(N11A) ··· O(5) 107(11)°], respectively. These distances are a little longer than the value of 2.876(8) Å expected for a typical hydrogen bond and both N–H ··· O angles are also smaller than that (143.1°) expected for a typical hydrogen bond.[4] In fact, a marked downfield shift of one of the amine protons, indicative of the presence of an intramolecular hydrogen bond,[4] was not observed in the ^1H NMR spectrum of complex **1** [Fig. 6(*a*)].

Crystal Structure of sym-$[\{Co(en)_2\}_2(\mu\text{-ttcy})][ClO_4]_3\cdot 2H_2O$ **4**.—Fig. 5 shows the projected top and side views of complex **4**. The numbering scheme is the same as that for complex **1** except for S(3) instead of O(5). The atomic parameters are listed in Table 4. The bond distances and angles obtained by the average of chemically equivalent bonds are shown in Fig. 4(*c*) while

Table 4 Positional parameters (× 10^4) for complex **4**

Atom	*x*	*y*	*z*
Co(1)	2471(1)	1555(1)	2886(1)
Co(2)	2484(1)	1269(1)	−1287(1)
S(1)	1927(3)	2700(3)	−1148(3)
S(2)	1859(3)	2926(3)	2476(3)
S(3)	3219(3)	149(3)	919(3)
N(1)	1944(8)	2898(7)	665(8)
N(2)	2546(7)	1668(7)	1585(8)
N(3)	2531(7)	1556(7)	−4(7)
N(4)	2184(8)	1630(8)	4131(8)
N(5)	1250(8)	962(7)	2695(8)
N(6)	3709(8)	2088(8)	3102(8)
N(7)	3114(8)	393(8)	3051(8)
N(8)	2223(8)	1205(8)	−2588(8)
N(9)	1231(8)	792(8)	−1177(9)
N(10)	3757(7)	1705(8)	−1419(8)
N(11)	3053(8)	60(8)	−1245(8)
C(1)	2160(9)	2421(9)	−53(9)
C(2)	2120(9)	2494(9)	1458(9)
C(3)	2745(9)	1177(9)	821(10)
C(4)	1156(12)	1522(12)	4233(12)
C(5)	821(11)	835(13)	3577(11)
C(6)	4415(11)	1364(13)	3050(14)
C(7)	4064(12)	534(11)	3471(13)
C(8)	1324(13)	706(18)	−2790(14)
C(9)	750(15)	813(18)	−2055(16)
C(10)	4410(12)	981(12)	−1146(14)
C(11)	4048(11)	93(11)	−1509(13)
Cl(1)	4557(3)	3386(3)	739(3)
Cl(2)	4304(4)	2254(4)	−3972(4)
Cl(3)	2430(4)	4266(3)	4460(4)
O(1)	3897(13)	3849(15)	236(17)
O(2)	5425(8)	3791(10)	726(9)
O(3)	4301(14)	3456(16)	1624(11)
O(4)	4526(12)	2557(15)	468(21)
O(5)	4278(24)	2024(16)	−4787(14)
O(6)	4639(23)	3092(17)	−3925(18)
O(7)	4662(18)	1675(18)	−3323(13)
O(8)	3454(20)	2327(25)	−3779(33)
O(9)	1840(12)	3548(9)	4604(11)
O(10)	3271(12)	3913(12)	4071(11)
O(11)	1919(15)	4810(12)	3803(15)
O(12)	2638(15)	4715(15)	5216(15)
O(W13)	3470(11)	4075(10)	−2136(13)
O(W14)	1786(14)	3084(12)	−3305(12)

individual bond lengths and angles around the cobalt centres are summarized in Table 3.

The bridging ttcy ligand is quadridentate using two symmetric N,S-donor sets. The bond length between the C atom (with non-co-ordinated substituent) and its substituent atom is 1.67(1) Å which corresponds to a normal C=S bond length.

The absolute configurations about Co(1) and Co(2) are Δ and Λ, respectively and complex **4** is *meso* like complex **1**. The three en chelate rings also adopt the *ob* conformation to the pseudo-C_3 axis but one en chelate ring has a *lel* (parallel) conformation.[14] In this complex two intramolecular hydrogen bonds were found between S(3) and N–H of en (*ob* form). The intramolecular distances N(7)···S(3) and N(11)···S(3) are 3.19(1) Å [H(16)···S(3) 2.20(17) Å, N(7)–H(16)···S(3) 155(13)°] and 3.21(1) Å [H(31)···S(3) 2.25(15) Å, N(11)–H(31)···S(3) 144(11)°], respectively. They are considerably shorter than the sum of the van der Waals radii (N–H···S 3.40 Å)[15] and are comparable with the 3.174(9) Å distance found in $[Co(dtuc)(en)_2]^{+}$[5] despite a double hydrogen bond structure in the present complex. Both N–H···S angles are high enough for an effective intramolecular hydrogen bond.[5] As shown in Fig. 6(*b*), complex **4** shows one downfield amine proton signal at δ 7.2 with the remainder signals at δ 3.9–5.6. This means that the two intramolecular N–H···S hydrogen bonds are retained even in $(CD_3)_2SO$ solution.

Comparison of the Structures of Complexes **1** *and* **4**.—Fig. 4(*a*) and 4(*c*) compare the structures of the bridging region of complexes **1** and **4**. In complex **1** the dtcy ligand has a delocalized electronic structure over the N(2)–C(2)–N(1)–C(1)–N(3) skeleton and only two bonds C(3)–N(2) and C(3)–N(3) are long, whereas in complex **4** only two bonds C(1)–N(1) and N(1)–C(2) are shorter than the other four bonds. The N(2)–C(3)–N(3) angle of complex **4** [118(1)°] is considerably larger than the corresponding angle of complex **1** [112(1)°]. Such structural differences probably relate to the reactivity of the ttcy ligand.

Projected top- [Fig. 5(*a*) and 5(*b*)] and side-views [Fig. 5(*c*) and 5(*d*)] of complexes **1** and **4** are shown in Fig. 5.

There is a difference in the orientation of two Co–N(en) axes parallel to the C=O and C=S groups as shown in Fig. 5(*a*) and 5(*b*). The average S–Co–N(en) angle 171.3(4)° in complex **4** is also larger than that [167.8(4)°] in complex **1**. Since the upper parts of the structures in Fig. 5(*a*) and 5(*b*) are almost the same, the difference exists in the lower parts. The Co(1)–N(7) and Co(2)–N(11) axes bend towards the C=O group in complex **1**, whereas they bend away from the C=S group in complex **4**. These facts may be ascribed to the larger van der Waals radius of the sulfur.

There is a further difference between **1** and **4** as evident in the side views of Fig. 5(*c*) and 5(*d*). In complex **1**, three planes, plane 1 [Co(1), S(2), N(4) and N(7)], plane 2 [C(1), N(1), C(2), N(2), C(3) and N(3)] and plane 3 [Co(2), S(1), N(8) and N(11)], form a large flat plane with a dihedral angle between planes 1 and 3 of only 7.8(5)°. In contrast, the corresponding three planes of complex **4** do not form a co-plane. The dihedral angle between plane 1 and plane 3 is 23.5(3)° for complex **4**. The non-bonded distances N(9)···N(5), Co(1)···Co(2) and N(10)···N(6) are 6.237(17), 6.082(3) and 6.020(17) Å for complex **1** and 5.741(17), 6.198(3) and 6.726(17) for complex **4**, respectively. It is of interest that the change of one non-co-ordinated substituent atom from 'the oxygen atom of dtcy' to 'the sulfur atom of ttcy' causes such a large structural deviation in complex **4**.

The Novel Desulfurization Reaction of ttcy.—The X-ray crystal analysis of complex **1** showed clearly the presence of the dtcy ligand, which is formed by a desulfurization reaction in which the sulfur atom of the ttcy ligand is replaced by oxygen. The fact that the yield of the dtcy complex (33%) is considerably higher than that of the ttcy complex (15%) is surprising. No precipitate corresponding to eliminated sulfur or any sulfide compound was observed immediately after irradiation, but a small amount of black precipitate appeared after 2 d upon standing of the reaction solution at room temperature. This precipitate may contain the eliminated sulfur, although we could not identify it.

In this preparation, dark red crystals (complex **5**) were also obtained in 40% yield. This complex is assigned to the mononuclear molecular complex $[Co(ttcy)(en)_2]$. However, the corresponding mononuclear dtcy complex $[Co(dtcy)(en)_2]$ was not identified either as crystals or in solution. These facts suggest that the desulfurization reaction does not occur in the ttcy ligand itself or in the mononuclear complexation process. Thus the reaction is reasonably inferred to occur only in the dinuclear complexation process.

Some typical desulfurization reactions are known so far: *e.g.* formation of $[\{MoS(SCNPr^n_2)(S_2CNPr^n_2)\}_2]$ by the oxidative cleavage of a dithiocarbamate C–S bond,[16] reductive desulfurization by organomercury compounds[17] and bromine-induced desulfurization in $[Cr(H_2O)_4L]$ [L = adenosine 5′-(2-thiotriphosphate)].[18] To our knowledge, the present desulfurization reaction with the simultaneous replacement by oxygen, under relatively mild conditions, is quite novel.

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