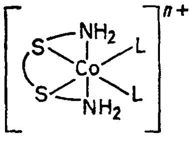
Cobalt(III) Complexes of 3,7-Dithianonane-1,9-diamine

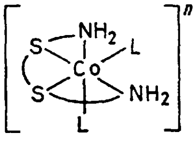
By **Robert W. Hay,* Peter M. Gidney, and Geoffrey A. Lawrance,** Chemistry Department, University of Stirling, Stirling FK9 4LA

A convenient synthetic route to the ligand 3,7-dithianonane-1,9-diamine (dtnd) has been developed. A series of cobalt(III) complexes, $[Co(dtnd)Cl_2]^+$, $[Co(dtnd)O_3C]^+$, $[Co(dtnd)(NO_2)_2]^+$, $[Co(dtnd)(NO_2)Cl]^+$, $[Co(dtnd)(NO_2)Br]^+$, $[Co(dtnd)(ox)]^+$ (ox = oxalate), with a variety of anions have been prepared and characterised. The *cis*-complexes have the *cis*-β-configuration in contrast to the complexes of 3,6-dithiaoctane-1,8-diamine (dtod) which give only the *cis*-α-isomers. In the case of $[Co(dtnd)Cl_2]^+$, both the *cis*-β- and the *trans*-isomers can be prepared. In the complex $[Co(dtnd)(NO_2)_2]^+$, one nitro-group is readily replaced by Cl^- or Br^- on treatment with the appropriate mineral acid. A recent crystal-structure determination on the complex $[Co(dtnd)(NO_2)Cl]Cl$ has shown that the nitro-group *trans* to the sulphur atom is displaced. The complex has the *cis*-β-configuration with the six-membered chelate ring in the chair conformation. The sulphur centres have the same chirality. N.m.r., i.r., and electronic spectra of the complexes are discussed.

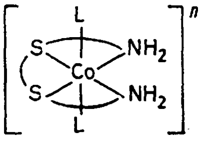
THERE has recently been considerable interest in the chemistry of sulphur–nitrogen ligands. Worrell and Busch[1] studied cobalt(III) complexes of 3,6-dithiaoctane-1,8-diamine (dtod).† Although three geometrical isomers are theoretically possible (I)—(III), the presence of the thioether donors leads to complete geometrical specificity and only the *cis*-α-isomers were isolated. The complexes, *cis*-α-$[Co(dtod)Cl_2]Cl$ and *cis*-α-$[Co(dtod)(NO_2)_2]Cl$, have been resolved and their optical-rotatory dispersion and circular-dichroism spectra studied.[2] Worrell *et al.*[3] showed that stereoselectivity, similar to that observed with propylenediaminetetra-acetic acid (pdta), is exhibited by (±)-4-methyl-3,6-dithiaoctane-1,8-diamine (mdtod) on co-ordination to cobalt(III). Optically pure $(+)_{589}$-mdtod and $(-)_{589}$-mdtod were recovered from the optically pure complexes D-*cis*-α-$(+)_{546}[Co(mdtod)Cl_2]Cl$ and L-*cis*-α-$(-)_{546}$-$[Co(mdtod)Cl_2]Cl$ respectively. The ligand mdtod shows complete geometrical and optical stereoselectivity. Some studies of cobalt(III) complexes of dtnd (3,7-dithianonane-1,9-diamine) were made by Bosnich *et al.*[4] These workers established that, in contrast to the dtod ligand which gave only the blue *cis*-α-$[Co(dtod)Cl_2]^+$ isomer, the dtnd ligand gave the green *trans*-$[Co(dtnd)Cl_2]^+$ and the red-violet *cis*-β-$[Co(dtnd)Cl_2]^+$ isomers. The stereochemistry of the complexes was discussed in terms of the conformations of the chelate rings. Recently Tobe and Tucker[5] studied the acid and base hydrolysis of *trans*-$[Co(dtnd)Cl_2]^+$.



cis-α
(I)



cis-β
(II)



trans
(III)

EXPERIMENTAL

The ligand 3,7-dithianonane-1,9-diamine (dtnd) was first prepared by Dwyer *et al.*[6] by the reaction of propane-1,3-dithiol with *N*-β-bromoethylphthalimide in the presence of sodium ethoxide. The resulting bis(phthalimido)-compound was hydrolysed with hydrazine and concentrated hydrochloric acid to give the dihydrochloride. This route, although costly, is still the most efficient means of preparing 3,6-dithiaoctane-1,8-diamine (dtod) if ethane-1,2-dithiol is used as the nucleophile. A much simpler route is to treat two equivalents of 2-aminoethanethiol (mercaptoethylamine) with one equivalent of 1,2-dibromoethane (for

---

† The ligands 3,7-dithianonane-1,9-diamine and 3,6-dithiaoctane-1,8-diamine are commonly abbreviated in the literature to ete and eee respectively. The present nomenclature is in accord with that recommended by the IUPAC authorities.

[1] J. H. Worrell and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1563.

[2] J. H. Worrell and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1572.

[3] J. H. Worrell, T. E. MacDermott, and D. H. Busch, *J. Amer. Chem. Soc.*, 1970, **92**, 3317.

[4] B. Bosnich, W. R. Kneen, and A. T. Phillip, *Inorg. Chem.*, 1969, **8**, 2567.

[5] M. L. Tobe and M. L. Tucker, *Inorg. Chem.*, 1973, **12**, 2994.

[6] F. P. Dwyer, F. Lions, and D. P. Mellor, *J. Amer. Chem. Soc.*, 1950, **72**, 5037.

dtod) or 1,3-dibromopropane (for dtnd) in the presence of two equivalents of sodium ethoxide. This route gave yields of *ca.* 40% (dtod), but yields of 75—80% for dtnd. The expensive 2-aminoethanethiol hydrochloride is readily prepared by acid hydrolysis of the readily available thiazoline-2-thione.

2-Aminoethanethiol Hydrochloride.—Thiazoline-2-thione (Aldrich, 100 g) was heated under reflux with hydrochloric acid (500 cm^3, 11·6M) for 400 h.* The resulting colourless solution was evaporated to dryness. 2-Aminoethanethiol hydrochloride was obtained as a colourless hygroscopic solid, m.p. 67—70 °C (lit.,[7] 70 °C), yield 87%.

3,7-*Dithianonane*-1,9-*diamine*.—To a solution of sodium (25·4 g, 1·1 g–atom) in absolute ethanol (400 cm^3), was added, with stirring under nitrogen, 2-aminoethanethiol hydrochloride (67·5 g, 0·6 mol). The mixture was heated under reflux and a solution of 1,3-dibromopropane (50 g, 0·25 mol) and sodium iodide (75 g, 0·5 mol) in absolute ethanol (300 cm^3) added dropwise. When the addition was complete (*ca.* 3 h) the mixture was heated under reflux with stirring under nitrogen for 20 h. After cooling and filtration the solvent was removed on a rotary evaporator. Any sodium salts which precipitated during the evaporation were removed by filtration. The residual oil was treated with water (50 cm^3) and the mixture extracted with chloroform (8 × 100 cm^3). The chloroform extracts were combined, dried over anhydrous sodium sulphate, and the chloroform removed on a rotary evaporator to give 3,7-dithianonane-1,9-diamine as a pale yellow oil, yield 44 g (95% based on 1,3-diaminopropane). This crude material was quite satisfactory for preparation of the cobalt(III) complexes. The ligand was stored in a desiccator over sodium hydroxide pellets as the amine rapidly absorbed water vapour and carbon dioxide from the air. During a period of weeks the crude amine darkens and slowly decomposes. The analytical data on the crude ligand were rather poor (Found: C, 41·3; H, 9·0; N, 13·5. Calc. for $C_7H_{18}N_2S_2$: C, 43·3; H, 9·3; N, 14·5%). The ligand can be purified by vacuum distillation, b.p. 168—175 °C at 1 mmHg, 144—148 °C at 0·5 mmHg (lit.,[6] 147 °C at 0·7 mmHg), to give a very pale yellow oil, which solidified on standing in a refrigerator but slowly melted at room temperature; ν(NH) at 3 360 and 3 275, δ(NH) at 1 590 cm^{-1} (liquid film), ^{1}H n.m.r. (δ/p.p.m., $CDCl_3$) NH_2 1·44 (4 H, S) and CH_2 2·4—2·9 (14 H, complex). The NH_2 protons exchanged in *ca.* 1 min on addition of D_2O (Found: C, 43·1; H, 9·2; N, 14·4. Calc. for $C_7H_{18}N_2S_2$: C, 43·3; H, 9·3; N, 14·5%).

cis-β-(3,7-*Dithianonane*-1,9-*diamine*)*dinitrocobalt*(III) *Chloride*, cis-β-$[Co(dtnd)(NO_2)_2]Cl$.—Cobalt(II) chloride hexahydrate (7·1 g) was dissolved in ethanol (25 cm^3) and warmed to 40 °C. To this solution was added, with stirring, crude 3,7-dithianonane-1,9-diamine (5·7 g) with concentrated hydrochloric acid (2·5 cm^3) in water (10 cm^3). Heating and stirring were continued and a stream of air was drawn through the mixture. Sodium nitrite (2·8 g) in water (20 cm^3) was added and heating and aeration continued. After a few minutes the suspension became brown. Additional sodium nitrite (1 g) in water (5 cm^3) was added and aeration continued for a further 15 min, with the mixture still maintained at 40 °C. The solution was allowed to cool, concentrated hydrochloric acid (2 cm^3) added, the ethanol removed on a rotary evaporator, and the resulting brown solution allowed to stand. After *ca.* 2 d the crude complex was filtered off and recrystallised by dissolving in hot water (400 cm^3) containing sodium nitrate (0·5 g), filtering, and evaporating the solution to *ca.* 50 cm^3. The red-brown complex so obtained was recrystallised from hot water (400 cm^3) containing concentrated hydrochloric acid (1 cm^3), yield 4·1 g, 36% (Found: C, 22·1; H, 4·9; N, 14·5; S, 16·9. Calc. for $C_7H_{18}ClCoN_4O_4S_2$: C, 22·1; H, 4·8; N, 14·7; S, 16·8%). The filtrates from the recrystallisations were combined with the mother liquor from the reaction mixture and evaporated to give further crude product (2 g).

cis-β-(3,7-*Dithianonane*-1,9-*diamine*)*dinitrocobalt*(III) *Perchlorate*, cis-β-$[Co(dtnd)(NO_2)_2][ClO_4]$.—The above chloride salt (0·4 g) was dissolved in warm water (50 cm^3). The resulting solution was filtered, treated with sodium perchlorate (0·2 g) in water (5 cm^3), and the solution evaporated to *ca.* 15 cm^3 (rotary evaporator), when the fluffy orange *product* crystallised. The complex was filtered off, washed with methanol then diethyl ether, and air dried (Found: C, 19·1; H, 4·0; N, 12·5. Calc. for $C_7H_{18}ClCoN_4O_8S_2$: C, 18·9; H, 4·1; N, 12·6%).

trans(S,Cl)-cis-β-*Chloro*(3,7-*dithianonane*-1,9-*diamine*)-*nitrocobalt*(III) *Chloride*, cis-β-$[Co(dtnd)(NO_2)Cl]Cl$.—The complex *cis*-β-$[Co(dtnd)(NO_2)_2]Cl$ (1·0 g) was dissolved in hot water (80 cm^3). The resulting solution was filtered, treated with concentrated hydrochloric acid (5 cm^3), and heated on a steam-bath until it became dark red (*ca.* 10 min). The red solution was evaporated (rotary evaporator) to *ca.* 10 cm^3 and the crystalline *product* removed by filtration, yield 0·7 g (Found: C, 22·8; H, 4·9; N, 11·3. Calc. for $C_7H_{18}Cl_2CoN_3O_2S_2$: C, 22·7; H, 4·9; N, 11·4%). The complex can be recrystallised from hot methanol–water.

trans(S,Cl)-cis-β-*Chloro*(3,7-*dithianonane*-1,9-*diamine*)-*nitrocobalt*(III) *Perchlorate*, cis-β-$[Co(dtnd)(NO_2)Cl][ClO_4]$.—This salt was prepared as above except that to the hot dark red solution was added sodium perchlorate (0·5 g) dissolved in the minimum volume of water. The resulting solution was evaporated to *ca.* 40 cm^3 (rotary evaporator) when the complex crystallised on cooling in ice (Found: C, 19·5; H, 4·3; N, 9·5. Calc. for $C_7H_{18}Cl_2CoN_3O_6S_2$: C, 19·4; H, 4·2; N, 9·7%).

cis-β-(3,7-*Dithianonane*-1,9-*diamine*)*dinitrocobalt*(III) *Bromide Monohydrate*, cis-β-$[Co(dtnd)(NO_2)_2]Br\cdot H_2O$.—The salt *cis*-β-$[Co(dtnd)(NO_2)_2]Cl$ (1·0 g) was dissolved in hot water (80 cm^3). The resulting solution was filtered, treated with sodium bromide (0·3 g) in water (5 cm^3), and evaporated to *ca.* 40 cm^3 (rotary evaporator) when the product crystallised, yield 1·0 g (Found: C, 19·0; H, 4·7; N, 12·6. Calc. for $C_7H_{20}BrCoN_4O_5S_2$: C, 19·0; H, 4·6; N, 12·6%).

trans(S,Br)-cis-β-*Bromo*(3,7-*dithianonane*-1,9-*diamine*)-*nitrocobalt*(III) *Bromide Dihydrate*, trans(S,Br)-cis-β-$[Co(dtnd)(NO_2)Br]Br\cdot H_2O$.—The salt *cis*-β-$[Co(dtnd)(NO_2)_2]Br\cdot H_2O$ (1·0 g) was dissolved in hot water (120 cm^3). The solution was filtered, treated with hydrobromic acid (5 cm^3, 48%), and heated on a steam-bath until the solution became dark red (*ca.* 10 min). The red solution was evaporated to *ca.* 25 cm^3 (rotary evaporator) and cooled in ice. The dark red *product* slowly crystallised, yield 0·55 g (Found: C, 17·2; H, 4·2; N, 8·3. Calc. for $C_7H_{22}Br_2CoN_3O_4S_2$: C, 17·0; H, 4·5; N, 8·5%). The i.r. spectrum confirmed the presence of water of crystallisation. Recrystallisation from hot methanol–water containing added sodium bromide gave the anhydrous complex.

---

* 1M = 1 mol dm^{-3}.

[7] R. J. Gaul and W. J. Fremuth, *J. Org. Chem.*, 1960, **25**, 869.

The complex can also be prepared from $[Co(dtnd)(NO_2)_2]Cl$ in a manner analogous to the preparation just described.

trans(S,Br)-cis-β-*Bromo*(3,7-*dithianonane*-1,9-*diamine*)-*nitrocobalt*(III) *Perchlorate,* trans(S,Br)-cis-β-$[Co(dtnd)(NO_2)Br][ClO_4]$.—The complex *trans*(S,Cl)-*cis*-β-$[Co(dtnd)(NO_2)Br]Br{\cdot}2H_2O$ was dissolved in cold water and passed down an anion-exchange column in the perchlorate form (Amberlite, *ca.* 50 g dry weight) and eluted with water. The red eluate was collected in a receiver cooled in ice. The solution was evaporated *in vacuo* to give reddish purple crystals (Found: C, 17·7; H, 4·2; N, 8·4. Calc. for $C_7H_{18}BrClCoN_3O_6S_2$: C, 17·6; H, 3·8; N, 8·8%).

cis-β-*Carbonato*(3,7-*dithianonane*-1,9-*diamine*)*cobalt*(III) *Perchlorate,* cis-β-$[Co(dtnd)CO_3][ClO_4]$.—*trans*(S,Cl)-*cis*-β-$[Co(dtnd)(NO_2)Cl]Cl$ (0·9 g) was mixed with a concentrated solution of ammonium carbonate (30 cm^3) and the mixture warmed on a water-bath for *ca.* 15 min, when the colour changed from purple-red to bright red. The reaction mixture was cooled in ice, ethanol added, and the precipitated ammonium salts removed by filtration. The volume was then reduced to *ca.* 5 cm^3 on a rotary evaporator, and concentrated sodium perchlorate solution added followed by ethanol (50 cm^3). The solution was refrigerated for several days when the *product* crystallised as dark red-purple needles; these were filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (0·12 g, 15%). The complex can be recrystallised from methanol–water (Found: C, 23·0; H, 4·4; N, 7·0. Calc. for $C_8H_{18}ClCoN_2O_7S_2$: C, 23·3; H, 4·4; N, 6·8%).

cis-β-(3,7-*Dithianonane*-1,9-*diamine*)*oxalatocobalt*(III) *Perchlorate Hydrate,* cis-β-$[Co(dtnd)(ox)][ClO_4]{\cdot}H_2O$.—The ion *cis*-β-$[Co(dtnd)(O_3C)]^+$ was prepared *in situ* from *trans*-(S,Cl)-*cis*-β-$[Co(dtnd)(NO_2)Cl]Cl$ (0·4 g) by warming on a water-bath with a concentrated solution (20 cm^3) of ammonium carbonate. The bright red solution so obtained was neutralised by the addition of solid oxalic acid. When evolution of carbon dioxide had ceased a slight excess of oxalic acid was added and the solution heated on a water-bath for 2 h. The cooled solution was filtered to remove ammonium oxalate and passed through a column of G-10 Sephadex. The major red band was eluted with water, collected, and reduced to small volume. Perchloric acid was added followed by ethanol (10 cm^3). The solution was cooled in an ice-bath for several hours and the bright red *product* filtered off, washed with ethanol then diethyl ether, and dried *in vacuo* (0·1 g, 20%). The complex can be recrystallised from water–ethanol (Found: C, 23·7; H, 4·4; N, 6·3. Calc. for $C_9H_{20}ClCoN_2O_9S_2$: C, 23·6; H, 4·4; N, 8·1%).

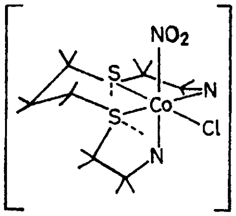
The salts *cis*-β-$[Co(dtnd)Cl_2][ClO_4]$ and *trans*-$[Co(dtnd)Cl_2][ClO_4]$ were prepared essentially as described by Bosnich *et al.*[4] (Found for the *cis*-isomer: C, 19·9; H, 4·4; N, 6·95. Found for the *trans*-isomer: C, 20·2; H, 4·4; N, 6·8. Calc. for $C_7H_{18}Cl_3CoN_2O_4S_2$: C, 19·9; H, 4·3; N, 6·6%).

N.m.r. spectra were determined using a Perkin-Elmer R-10 instrument, using $(D_3C)_2SO$ as solvent and $SiMe_4$ as internal standard. Electronic spectra were measured using a Perkin-Elmer 402 instrument with either water or aqueous HBr–HCl as solvent. I.r. spectra were determined as discs (KBr) using a Perkin-Elmer 457 instrument.

RESULTS AND DISCUSSION

Octahedral metal complexes formed by the ligands dtod and dtnd can exist in potentially three isomeric forms: the *cis*-α-, *cis*-β-, and *trans*-isomers. In the case of dtod, if it is assumed that (*a*) each chelate ring will adopt a *gauche*-conformation and (*b*) that the atoms will approximately retain their normal trigonal, tetrahedral, and octahedral bond angles, it is possible to decide the most stable configuration. Molecular models show that for dtod the only configuration which satisfies both these criteria is the *cis*-α-isomer. In either the *cis*-β- or *trans*-stereochemistry considerable strain is produced in the system, the *trans*-isomer being more strained than the *cis*-β-isomer. Since only the *cis*-α-isomers of dtod have been prepared, it is clear that the criteria (*a*) and (*b*) are of major importance in deciding the stereochemistry of these systems.

The situation with regard to dtnd is more complicated because of the presence of the central six-membered chelate ring. The latter can adopt either a pseudo-chair or a number of pseudo-boat conformations (chair, boat, and skew). Bosnich *et al.*[4] assumed that the order of decreasing stability for these three conformers is chair > skew > boat. The crystal structure of $[Co(dtnd)(NO_2)Cl]Cl$ obtained by treating $[Co(dtnd)(NO_2)_2]^+$ with hydrochloric acid has recently been determined and shown to be as in (IV),[8] *i.e.* the chair-*cis*-β-*RR* configuration with the Cl ligand *trans* to sulphur. Both sulphur donors have the same chirality. All the *cis*-complexes have the *cis*-β-configuration, and this conclusion is confirmed by the n.m.r. results in Table 1. Of the four N–H protons in these complexes, two pairs are environmentally equivalent in the *cis*-α-geometry, no two are equivalent in the *cis*-β-geometry, and all are essentially equivalent in the *trans*-geometry.



trans (S,Cl)–chair–*cis*–β–*RR*

(IV)

The complex most readily obtained in high yield was *cis*-β-$[Co(dtnd)(NO_2)_2]Cl$. Treatment of the dinitro-complex with hydrochloric or hydrobromic acid gave the corresponding chloronitro- and bromonitro-complexes. The dichloro-complex can only be prepared by removing nitrous acid–nitrite with urea. If any nitrite is present the halogenonitro-complex is isolated. The crystal structure of *cis*-β-$[Co(dtnd)(NO_2)Cl]Cl$ confirms that the labile nitro-group lies *trans* to sulphur. It would be expected that the *trans*-effect of sulphur would be greater than that of nitrogen. Elder *et al.*[9] showed that there is a significant lengthening of the *trans* cobalt–nitrogen bond length when a sulphur donor is

---

[8] J. Murray-Rust and P. Murray-Rust, *Acta Cryst.*, 1973, **B29**, 2606.

[9] R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, 1973, **12**, 2690.

present. The equilibrium between *trans*- and *cis*-β-[Co(dtnd)Cl_2]$^+$ was studied spectrophotometrically at 80 °C in 2M-hydrochloric acid. Both complexes gave essentially the same spectrum, after equilibration, corresponding to *ca.* 60% *cis*-β- and 40% *trans*-[Co(dtnd)Cl_2]$^+$. There was a small standing concentration of the aquachloro-species (*ca.* 3%). It seems probable that the complexes isomerise *via* the aquachloro-species. The standard free-energy difference $\Delta G_{353}^{\ominus}$ is thus *ca.* 1·2 kJ mol^{-1}.

TABLE 1

N.m.r. spectra in $(D_3C)_2SO$ *

τ	Relative intensity		Assignment
	Obs.	Calc.	
trans(S,Cl)-*cis*-β-[Co(dtnd)(NO_2)Cl][ClO_4]			
3·82, 3·96	1·0	1	NH
4·50	1·0	1	NH
5·26	0·6	1	NH
5·95, 6·13	0·8	1	NH
6·4—8·4 (complex)	14·6	14	CH_2
cis-β-[Co(dtnd)$(NO_2)_2$][ClO_4]			
3·86, 4·03	1·0	1	NH
5·08	1·8	1 + 1	NH
6·03, 6·21	0·8	1	NH
6·4—8·4 (complex)	14·7	14	CH_2
trans(S,Br)-*cis*-β-[Co(dtnd)(NO_2)Br][ClO_4]			
3·66, 3·82			NH
4·51			NH
5·06			NH
5·88, 6·06			NH
6·4—8·2 (complex)			CH_2

* The spectra were recorded on a Perkin-Elmer R-10 instrument and accumulated 25 times using a Digiac computer. The accumulated spectra were then integrated. For the bromonitro-derivative the peaks were too weak for satisfactory integration.

Base hydrolysis of the halogeno-ligands occurs rapidly, but base-catalysed decomposition of the organic ligand also takes place. Base hydrolysis of *trans*-[Co(dtnd)Cl_2]$^+$ has recently been studied in detail by Tobe and Tucker.[5] Similar observations apply to *trans*(S,Cl)-*cis*-β-[Co(dtnd)(NO_2)Cl]$^+$. In 0·05M-$Na_2B_4O_7$·$10H_2O$ buffer, $\lambda_{max.}$, initially at 522 nm, moved slowly to 504 nm, but a clean isosbestic point was not observed and a stable final spectrum was not obtained. Both the bromonitro- and the chloronitro-complexes react with ammonium carbonate solution on warming to give red-purple *cis*-β-[Co(dtnd)(O_3C)]$^+$ which can be isolated as the perchlorate salt. The bidentate carbonate group gave rise to characteristic bands at 1 655, 1 630, 1 610, and 823 cm^{-1}. The carbonato-complex can be treated with a slight excess of oxalic acid in aqueous solution to give red *cis*-β-[Co(dtnd)(ox)]$^+$ which can be crystallised as the perchlorate hydrate. This complex has characteristic ν(CO) bands at 1 700, 1 679, and 1 660 cm^{-1}. The *cis*-β-[Co(dtnd)$(NO_2)_2$]Cl complex exhibits an N–O asymmetric stretch at 1 384 cm^{-1} and a symmetric N–O stretch at 1 350 cm^{-1}. The O–N–O deformation is a multiplet at 822 and 818 cm^{-1}. In the bromonitro- and chloronitro-complexes a single band occurs at 822 cm^{-1}. Characteristic i.r. bands of the complexes are listed in Table 2. It is worthy of note that the i.r. data for the *cis*-α-[Co(dtod)X_2]$^{n+}$ and *cis*-β-[Co(dtnd)X_2]$^{n+}$ derivatives are very similar and it would be difficult to deduce geometry from these data alone.

Worrell and Busch[1] pointed out that it should be possible to distinguish the *cis*-α-configuration from the *cis*-β- on the basis of electronic spectra. For the

TABLE 2

I.r. spectra (cm^{-1}) of the complexes *

Complex	$\bar{\nu}$(NH,OH)	$\bar{\delta}$(NH,OH)	$\bar{\nu}$(CH)	Other
cis-β-[Co(dtnd)(NO_2)]Cl	3 196s	1 592m	3 000w	1 384s N–O (asym)
	3 130s, b	1 574m	2 972w	1 350w N–O (sym)
	3 062vs, b			822m, 818m } O–N–O (def)
				675w ν(CS)
cis-β-[Co(dtnd)(NO_2)Br]Br·$2H_2O$	3 280s, b	1 636m	2 985w	1 384s N–O (asym)
	3 220m, b	1 615m		1 354w N–O (sym)
	3 160s, b	1 601m		822s O–N–O (def)
	3 100s, b	1 580m		665w ν(CS)
cis-β-[Co(dtnd)(NO_2)Cl]Cl	3 190m, b	1 590m	3 000w	1 375s N–O (asym)
	3 150m, b	1 578m	2 960w	1 60w N–O (sym)
	3 050s, b		2 925w	822s O–N–O (def)
				670w ν(CS)
cis-β-[Co(dtnd)(O_3C)][ClO_4]	3 280s, b	1 595s	3 000w	1 655s
	3 235s, b		2 930w	1 630vs } $[CO_3]^{2-}$
	3 145s, b			1 610vs
				823 π-$[CO_3]^{2-}$
				675w ν(CS)
cis-β-[Co(dtnd)(ox)][ClO_4]·H_2O	3 420s, b	1 576m	3 000w	1 700vs
	3 260s, b		2 945w	1 679vs } ox^{2-}
	3 190s, b		2 925w	1 660s
	3 110s, b			670w ν(CS)
cis-β-[Co(dtnd)Cl_2][ClO_4]	3 295s	1 590m	3 000w	665w ν(CS)
	3 240s	1 575s	2 980w	
	3 180s	1 560w		
	3 115s			
trans-[Co(dtnd)Cl_2][ClO_4]	3 310s	1 584s	3 000w	670w ν(CS)
	3 240s	1 540m	2 940w	
	3 140m, b			

* All spectra were determined as KBr discs.

TABLE 3

Complex	Solvent	λ/nm	ε/l mol^{-1} cm^{-1}
cis-β-[Co(dtnd)(NO_2)$_2$]Cl	H_2O	464	640
		345	7 700
		270	15 300
cis-β-[Co(dtnd)(NO_2)Cl]Cl	0·1M-HCl	522	378
		350 (sh)	3 730
		278	14 300
cis-β-[Co(dtnd)(NO_2)Br]Br·2H_2O	0·1M-HBr	530	331
		348 (sh)	3 640
		280	10 800
[Co(dtnd)(O_3C)][ClO_4]	H_2O	524	387
		368 (sh)	485
[Co(dtnd)(ox)][ClO_4]·H_2O	H_2O	516	315
		382	390
cis-β-[Co(dtnd)Cl_2][ClO_4]	1M-HCl	537	246
		400 (sh)	346
trans-[Co(dtnd)Cl_2][ClO_4]	1M-HCl	630	58
		460 (sh)	97

cis-α-configuration, characteristic tetragonal splitting of the ${}^1T_{1g}$ state is expected, since the average in-plane (*xy*) ligand field will not be the same as the axial field along the *z* axis. In the *cis*-β-configuration the ${}^1T_1$ band would *not* be expected to be split, because the donor atoms of the quadridentate ligand and the two aniono-groups are positioned so as to result in three unique axial fields of comparable magnitude. Splitting is observed in *cis*-α-[Co(dtod)Cl_2]$^+$ and *cis*-α-[Co(dtdd)Cl_2]$^+$ (dtdd = 4,7-dithiadecane-1,10-diamine) while splitting is not observed with *cis*-β-[Co(dtnd)Cl_2]$^+$ or with *cis*-β-[Co(dtdd)Cl_2]$^+$ so that the electronic spectrum provides a useful diagnostic tool for the assignment of stereochemistry. The position of the ${}^1A_{1g}\rightarrow{}^1T_{1g}$ band does not vary markedly with stereochemistry, thus for *cis*-α-[Co(dtod)(NO_2)$_2$]$^+$ and *cis*-β-[Co(dtnd)(NO_2)$_2$]$^+$ the band occurs at 463 and 464 nm respectively and for *cis*-α-[Co(dtod)Cl_2]$^+$ and *cis*-β-[Co(dtnd)Cl_2]$^+$ at 610 and 537 nm.

We thank the S.R.C. for support.

[4/1304 *Received*, 1*st July*, 1974]