# 396. *Complexes of Tetrahydrothiophen Oxide.*

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The co-ordination chemistry of tetrahydrothiophen oxide with a variety of metal salts as acceptors has been investigated. New complexes have been isolated and characterized by analytical, magnetic, and spectral data. The stoicheiometric and stereochemical relationships parallel those with dimethyl sulphoxide.

WE have recently reported the preparation and characterization of a variety of complexes containing dimethyl sulphoxide as donor.[1-3] Our studies have been extended to the ligand behaviour of other sulphoxides, and in this paper we describe some complexes formed by the cyclic sulphoxide, tetrahydrothiophen oxide $[CH_2]_4{>}SO$ (referred to in formulæ below as Tpo). It was expected that despite the presence of a larger hydrocarbon residue bonded to the sulphur, the locking of the methylene groups in the ring would have a compensatory effect, making this sulphoxide at least as good a donor as dimethyl sulphoxide. Consistently with this we have found that metal salts generally are highly soluble in tetrahydrothiophen oxide and that the isolation of well-defined complexes is relatively easy.

It is evident from the types of complexes obtained and their properties that tetrahydrothiophen oxide has ligand behaviour fundamentally similar to that of dimethyl sulphoxide. The complex with boron trifluoride is analogous to those formed by dimethyl sulphoxide [1] and by n-dodecyl ethyl sulphoxide.[4] The ferric chloride and stannic chloride complexes possess the same high thermal stability as their dimethyl sulphoxide analogues.

The infrared data recorded in Table 1 are subject to the same interpretation as was previously developed [2] for dimethyl sulphoxide complexes, and they indicate that co-ordination takes place through the oxygen atom in all cases except for the palladium(II) and platinum(II) complexes, where it appears that the sulphur atom is bound to the metal. With tetrahydrothiophen oxide, the steric argument in favour of oxygen co-ordination in the hexakis(tetrahydrothiophen)metal(II or III) ions is, of course, even more cogent than for the analogous species containing dimethyl sulphoxide.

TABLE 1. *Infrared data for some tetrahydrothiophen oxide complexes.*

| Compound | S–O Stretching frequency (cm.$^{-1}$) | Compound | S–O Stretching frequency (cm.$^{-1}$) |
|---|---|---|---|
| $C_4H_4S$(Tetrahydrothiophen) [a] | No significant bands 650—1200 cm.$^{-1}$ | $[Co(Tpo)_6](CoI_4)$ [d] | 965s |
| $C_4H_4SO$(Tpo) [a] | 1010s * | $[Ni(Tpo)_6](NiCl_4)$ [b] | 971s |
| $[Co(Tpo)_6](ClO_4)_2$ [b] | 963s | $[Ni(Tpo)_4]Br_2$ [c] | 970s |
| $[Co(Tpo)_6](CoCl_4)$ [b] | 965s | $[Ni(Tpo)_4]I_2$ [d] | 945s |
| $[Co(Tpo)_6]Br_2$ [c] | 967s | $[Cu(Tpo)_2Cl_2]$ [b] | 937s |
| $[Co(Tpo)_6](CoBr_4)$ [c] | 966s | $[Pd(Tpo)_2Cl_2]$ [b] | 1127s † |
| $[Co(Tpo)_6]I_2$ [d] | 963s | $[Pt(Tpo)_2Cl_2]$ [b] | 1155 ‡ |

[a] 10% solution in $CHCl_3$. [b] Pressing in KCl. [c] Pressing in KBr. [d] Pressing in KI.
* Also 1150mw, 1092m, 660m. † Also 1140sh, 1068s. ‡ Also 1140m, 1130m, 1087m, 1077m.

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[1] Cotton and Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.
[2] Cotton, Francis, and Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.
[3] Cotton and Francis, *J. Inorg. Nuclear Chem.*, in the press.
[4] Laughlin, *J. Org. Chem.*, 1960, **25**, 864.

The cobalt and nickel complexes of tetrahydrothiophen oxide show the same stereochemical tendencies as do those of dimethyl sulphoxide [1,3] as comparison of the formulæ, properties, and interconversion sequences in the two series of compounds clearly shows. It seems safe to presume from their colours and evident stoicheiometric relations to the corresponding dimethyl sulphoxide compounds [1,3] that the tetrahydrothiophen oxide compounds may be assigned structures in the following way.

For $CoCl_2$,3Tpo, the structure should be $[Co(Tpo)_6][CoCl_4]$, in which the cation contains cobalt(II) octahedrally co-ordinated by oxygen atoms and the tetrachlorocobaltate(II) ion is, of course, tetrahedral. The apparent magnetic moment of the cobalt(II) in this compound, 4·89 B.M. at 28°, agrees with that previously reported for $CoCl_2$,3DMSO.[1,3] Similarly, there seems little doubt that $CoBr_2$,6Tpo and $CoBr_2$,3Tpo are correctly formulated as $[Co(Tpo)_6]Br_2$ and $[Co(Tpo)_6][CoBr_4]$, and $CoI_2$,6Tpo and $CoI_2$,3Tpo as $[Co(Tpo)_6]I_2$ and $[Co(Tpo)_6][CoI_4]$. The red colour of $Co(SCN)_2$,4Tpo indicates that it does not contain tetrahedrally co-ordinated cobalt(II) although the deep blue solution from which it crystallizes evidently does; octahedral, $[Co(Tpo)_4(SCN)_2]$, or planar, $[Co(Tpo)_4](SCN)_2$, structures are possible. The deep blue $Co(SCN)_2$,3Tpo is doubtless correctly formulated as $[Co(Tpo)_6][Co(NCS)_4]$. $[Co(Tpo)_6](ClO_4)_2$ has the high magnetic moment (Table 2) typical of many octahedral cobalt(II) compounds, as does $[Co(DMSO)_6](ClO_4)_2$.

TABLE 2. *Magnetic data for several complexes containing tetrahydrothiophen oxide.*[a]

| Compound | $\chi^{corr.}$ (c.g.s. units × $10^6$) | Diamag. (corr.) (c.g.s. units × $10^6$) | Temp. (° K) | $\mu^{(eff.)}$ [b] (B.M.) |
|---|---|---|---|---|
| $[Co(C_4H_8SO)_6](ClO_4)_2$ ............ | 10,420 | −438 | 301 | 5·03 |
| $[Co(C_4H_8SO)_6][CoCl_4]$ ............ | 9930 | −240 | 301 | 4·89 |
| $[Ni(C_4H_8SO)_6][NiCl_4]$............... | 5720 | −240 | 295 | 3·69 |
| $NiBr_2,4C_4H_8SO$ ..................... | 5950 | −323 | 296 | 3·77 |

[a] Molar susceptibilities are for a formula unit containing one metal ion, *e.g.*, for $[Co(C_4H_8SO)_6][CoCl_4]$ for the formula unit $CoCl_2,3C_4H_8SO$, and effective moments are per metal atom. [b] Calc. from the Curie equation.

The compounds $[Ni(Tpo)_6](ClO_4)_2$, $[Ni(Tpo)_6][NiCl_4]$, $[Ni(Tpo)_6]Br_2$, $[Ni(Tpo)_6][NiBr_4]$, $NiBr_2$,4Tpo, $[Ni(Tpo)_6]I_2$, $NiI_2$,4Tpo, and $Ni(SCN)_2$,4Tpo all have their dimethyl sulphoxide analogues. No dimethyl sulphoxide analogue of $[Ni(Tpo)_6]Cl_2$ was isolated, but it might be possible to do so; no particular attempt has been made by us. Once again the tetrahedral tetrachloronickelate(II) and tetrabromonickelate(II) ions are formed. The high mean magnetic moment of the nickel atoms in $[Ni(Tpo)_6][NiCl_4)$ gives definite confirmation of this, as shown previously [1,3] for the analogous dimethyl sulphoxide compound. The pale green colour of $Ni(SCN)_2$,4Tpo shows that this compound, like its dimethyl sulphoxide analogue,[3] does not contain tetrahedral nickel(II). Again in this series of compounds we obtain a bromide of the stoicheiometry $NiBr_2$,4 sulphoxide, which is blue and appears to contain all or some of its nickel ions in tetrahedral co-ordination. The magnetic moment of 3·77 BM supports this view, as does the appearance of the reflectance spectrum, which very closely resembles that of $NiBr_2$,4DMSO.

## EXPERIMENTAL

In formulæ, Tpo denotes tetrahydrothiophen oxide.

*Compound* $BF_3$,Tpo.—Gaseous boron trifluoride was passed into a benzene solution of tetrahydrothiophen oxide (Wateree Chemical Co., Lugoff, S. C.). An exothermic reaction occurred and, on cooling, colourless crystals of the *complex* separated. These were sublimed at 65° in a good vacuum (Found: C, 27·9; H, 4·8. $C_4H_8BF_3OS$ requires C, 27·9; H, 4·7%).

*Compound* $FeCl_3$,2Tpo.—Tetrahydrothiophen oxide was added dropwise to an ether solution of anhydrous (sublimed) ferric chloride, producing an immediate yellow precipitate; this *product* was filtered off, dried by pumping at room temperature, and sublimed at 170° in a good vacuum (Found: C, 25·5; H, 2·9. $C_8H_{16}Cl_3FeO_2S_2$ requires C, 25·9; H, 4·4%).

*Compound* $CuCl_2$,2Tpo.—Cupric chloride was dissolved in a 5 molar excess of warm tetrahydrothiophen oxide to give a green solution. Green crystals of the *salt*, which were slowly deposited, were separated and dried in vacuum at 55° (Found: C, 28·0; H, 4·8; Cl, 20·6; Cu, 18·5. $C_8H_{16}Cl_2CuO_2S_2$ requires C, 28·0; H, 4·7; Cl, 20·7; Cu, 18·5%).

*Compound* $SnCl_4$,2Tpo.—Tetrahydrothiophen oxide was added dropwise to undiluted stannic chloride, giving a white precipitate of *complex* which was filtered and sublimed at 210° in a high vacuum (Found: C, 20·3; H, 3·3. $C_8H_{16}Cl_4O_2S_2Sn$ requires C, 20·5; H, 3·4%).

*Compound* $PdCl_2$,2Tpo.—Palladium chloride was dissolved in about a 5-molar excess of warm tetrahydrothiophen oxide. From the yellow solution, a brown crystalline *product* separated on storage. It was dried in a vacuum at 55° (Found: C, 25·3; H, 4·3. $C_8H_{16}Cl_2O_2PdS_2$ requires C, 24·9; H, 4·2%).

*Compound* $PtCl_2$,2Tpo.—Tetrahydrothiophen oxide was added dropwise with agitation to a concentrated aqueous solution of hydrogen tetrachloroplatinate(II), warmed to 60°, until the deep red-orange colour was discharged to a light yellow. The volume was then reduced in a vacuum-desiccator until fine, pale yellow crystals of the *complex* separated. These were separated, twice recrystallized from water, and dried in a vacuum (Found: C, 20·4; H, 3·5. $C_8H_{16}Cl_2O_2PtS_2$ requires C, 20·2; H, 3·4%).

*Compound* $CoCl_2$,3Tpo.—Anhydrous cobaltous chloride was dissolved in a 10 molar excess of tetrahydrothiophen oxide to give a dark blue solution from which dark blue crystals of the *product* were obtained on removal of excess of tetrahydrothiophen oxide in a vacuum (Found: C, 32·7; H, 5·5; Cl, 16·0; Co, 13·3. $C_{12}H_{24}Cl_2CoO_3S_3$ requires C, 32·6; H, 5·5; Cl, 16·0; Co, 13·3%).

*Compounds* $CoBr_2$,6Tpo *and* $CoBr_2$,3Tpo.—Anhydrous cobaltous bromide dissolved in tetrahydrothiophen oxide to give a pink solution from which a pink crystalline product, *hexakis(tetrahydrothiophen oxide)cobalt*(II) *dibromide* (Found: C, 34·0; H, 5·7. $C_{24}H_{48}Br_2CoO_6S_6$ requires C, 34·2; H, 5·7%), separated when the solution was kept over phosphorus pentoxide. This complex was filtered off and dried in a vacuum at room temperature. When heated in a vacuum at 60° the pink substance loses tetrahydrothiophen oxide immediately, and a light blue powder, *tris(tetrahydrothiophen oxide)cobalt*(II) *dibromide*, is obtained (Found: C, 27·2; H, 4·7. $C_{12}H_{24}Br_2CoO_3S_3$ requires C, 27·1; H, 4·6%).

*Compounds* $CoI_2$,6Tpo *and* $CoI_2$,3Tpo.—Anhydrous cobaltous iodide was dissolved in tetrahydrothiophen oxide to give a pale yellow solution which became red-orange on concentration over phosphorus pentoxide in a vacuum. Deep red crystals of *hexakis(tetrahydrothiophen oxide)cobalt*(II) *iodide* separated (Found: C, 30·5; H, 5·1. $C_{24}H_{48}CoI_2O_6S_6$ requires C, 30·7; H, 5·2%). They were filtered off and dried in a vacuum at room temperature. In a vacuum at 60° they readily lost tetrahydrothiophen oxide, affording dark green *tris(tetrahydrothiophen oxide)cobalt*(II) *iodide* (Found: C, 23·0; H, 3·6. $C_{12}H_{24}I_2CoO_3S_3$ requires C, 23·0; H, 3·8%).

*Compounds* $Co(SCN)_2$,4Tpo *and* $Co(SCN)_2$,3Tpo.—Hexa-aquocobalt(II) thiocyanate was dissolved in a ten-fold molar excess of tetrahydrothiophen oxide, giving a pink solution. When kept over phosphorus pentoxide in a vacuum, this solution slowly became dark blue, while red crystals of *tetrakis(tetrahydrothiophen oxide)cobalt*(III) *dithiocyanate* separated. These were filtered off and dried in a vacuum at room temperature (Found: C, 26·8; H, 5·4. $C_{18}H_{32}CoN_2O_4S_6$ requires C, 36·5; H, 5·4%). In a vacuum at 60°, they lost tetrahydrothiophen oxide, affording dark blue *tris(tetrahydrothiophen oxide)cobalt*(II) *dithiocyanate* (Found: C, 34·3; H, 4·9. $C_{14}H_{24}CoN_2O_3S_5$ requires C, 34·5; H, 5·0%).

*Compound* $Co(ClO_4)_2$,6Tpo.—Hexa-aquocobalt(II) perchlorate was dissolved in tetrahydrothiophen oxide to give a pink solution. On removal of the excess of tetrahydrothiophen oxide in a vacuum, pink crystals of the *complex* were obtained (Found: C, 32·51; H, 5·45; Co, 6·7. $C_{24}H_{48}Cl_2CoO_{14}S_6$ requires C, 32·6; H, 5·5; Co, 6·7%).

*Compounds* $NiCl_2$,6Tpo *and* $NiCl_2$,3Tpo.—Anhydrous nickel chloride was dissolved in a ten-fold molar excess of tetrahydrothiophen oxide to give a pale green solution. On storage of this over phosphorus pentoxide in a vacuum, green crystals of *hexakis(tetrahydrothiophen oxide)nickel*(II) *dichloride* were deposited. These were filtered off and dried over phosphorus pentoxide in a vacuum at room temperature (Found: C, 38·5; H, 6·5. $C_{24}H_{48}Cl_2NiO_6S_6$ requires C, 38·2; H, 6·4%). In a vacuum at 60°, these crystals lost tetrahydrothiophen oxide, affording *tris(tetrahydrothiophen oxide)cobalt*(II) *dichloride* as a light blue-green powder (Found: C, 32·6; H, 5·7. $C_{12}H_{24}Cl_2NiO_3S_3$ requires C, 32·6; H, 5·47%).

*Compounds* $NiBr_2,6Tpo$, $NiBr_2,4Tpo$, *and* $NiBr_2,3Tpo$.—Anhydrous nickel bromide was dissolved in a ten-fold molar excess of tetrahydrothiophen oxide to give a light green solution which, when kept over phosphorus pentoxide in a vacuum, deposited green crystals of ***hexakis-(tetrahydrothiophen oxide)nickel*(II) *dibromide*** (Found: C, 33·7; H, 5·3. $C_{24}H_{48}Br_2NiO_6S_5$ requires C, 34·2; H, 5·7%). This rather easily loses tetrahydrothiophen oxide on long standing to give light blue *tetrakis(tetrahydrothiophen oxide)nickel*(II) *dibromide* (Found: C, 30·0; H, 5·0. $C_{16}H_{32}Br_2NiO_4S_4$ requires C, 30·2; H, 5·1%). On prolonged heating at 80° in a vacuum, both of the foregoing compounds lose tetrahydrothiophen oxide to give dark green *tris(tetrahydrothiophen oxide)nickel*(II) *dibromide* (Found: C, 27·4; H, 4·6. $C_{12}H_{24}Br_2NiO_3S_3$ requires C, 27·1; H, 4·6%).

*Compounds* $NiI_2,6Tpo$ *and* $NiI_2,4Tpo$.—Anhydrous nickel iodide was dissolved in tetrahydrothiophen oxide to give a pale orange solution which deposited light green crystals of hexakis(tetrahydrothiophen oxide)nickel(II) iodide on storage over phosphorus pentoxide in a vacuum. The analytical figures for this substance approximated to those required by the above formula, but were always somewhat low in carbon and hydrogen owing to the instability of the compound. When these green crystals were kept in air or were heated at 60° in a vacuum, they readily lost tetrahydrothiophen oxide, affording the red-orange compound *tetrakis(tetrahydrothiophen oxide)nickel*(II) *di-iodide* (Found: C, 26·1; H, 4·1. $C_{16}H_{32}I_2NiO_4S_4$ requires C, 26·4; H, 4·4%).

*Compound* $Ni(SCN)_2,4Tpo$.—Hydrated nickel thiocyanate was dissolved in tetrahydrothiophen oxide to give a light green solution which deposited a *complex* as light green crystals when kept over phosphorus pentoxide in a vacuum. No other definite compound was obtained on heating these green crystals in a vacuum (Found: C, 36·6; H, 5·3. $C_{18}H_{32}N_2NiO_4S_6$ requires C, 36·5; H, 5·4%).

*Compound* $Ni(ClO_4)_2,6Tpo$.—Hexa-aquonickel(II) perchlorate was dissolved in tetrahydrothiophen oxide, giving a green solution which afforded light green crystals of a *complex* when excess of tetrahydrothiophen oxide was distilled off in a vacuum (Found: C, 32·7; H, 5·4. $C_{24}H_{48}Cl_2NiO_{14}S_6$ requires C, 32·7; H, 5·5%).

All physical measurements were made as previously described.[1-3]

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