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Coordination Compounds with Thioxane Oxide and Thiacyclohexane Oxide as Ligands. Their Use in Determination of Coordination Numbers to Oxygen Ligands for Non-Transition Metal Cations[1]

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Thioxane oxide (TSO) and thiacyclohexane oxide (TCHO) were found to be good ligands for coordination to metal ions, both transition and non-transition. Many new compounds have been prepared. The results with the non-transition metal perchlorates are of particular interest because the ratio of bound sulfoxide molecules to metal cations gives information on the coordination number to oxygen of the metal ions.

Introduction

The coordination numbers of the transition metals are obtained with ease since the characteristic spectra of the complexes are readily interpretable and since these metals often form inert complexes in which the number of ligands remains constant through a series of reactions. For example, the aquo-chromium(III) ion in aqueous solution is known to have an octahedral hydrate coordination sphere on the basis of its spectra and of its isotope exchange properties.

The coordination numbers of the non-transition metals are less well-known for three reasons: (1) there are neither spectra of the d-d type nor magnetic properties to allow an interpretation of the molecular symmetry; (2) the rates of ligand replacement are much faster than normal chemical operations; and (3) many of the aquo complexes of these metal ions have strong tendencies to hydrolyze and polymerize thereby altering the structure. We felt, therefore, that some method involving chosen ligands might give useful information about the metal ion coordination numbers to oxygen. In two cases, involving mercuric ion[2] and uranyl ion,[3] our results have given substantiation to predictions in the literature. In the present paper, a large number of new compounds are presented, the bases for our choice of ligands and anions are discussed and some conclusions are drawn. The type of results obtained here should be considered a tentative indication of coordination number to monodentate oxygen ligands; individual cases of interest should be checked with a more definitive method such as X-ray. Nevertheless, the results do point to one way towards solution of the problem of aqueous coordination numbers of the non-transition elements.

Discussion of Factors

Choice of Ligand. In order to obtain a measure of success in evaluation of coordination numbers from stoichiometry of solid complexes, certain factors concerning the ligand must be considered. These are as follows: (1) the ligand should be one in which hydrolysis cannot occur as it can for alcohols ROH and water, (2) the ligand should be monodentate, for polydentate ligands can lead to higher coordination numbers (such as is the case where nitrate ion, carbonate ion, acetate ion, etc., bond through two oxygens which are closer together in the anion than could be two oxygen atoms on adjacent ligands) or to coordination numbers which are multiples of the dentation (with oxalate ion and ethylenediamine, even coordination numbers will usually be obtained), (3) the ligand should be electrically neutral — so that the negative charge does not build up with addition of ligands — particularly where the cation charge is small but the radius is large, (4) the ligand should have some property (such as an infrared band) which can be employed to show that all of the ligands present are in the coordination sphere, and (5) the bonding site of the ligand should have a relatively small bulk so that steric interaction between adjacent ligands in the complex will be negligible.

On the basis of these considerations, two groups of ligands seemed promising. Among the sulfoxides, four were chosen: dimethyl sulfoxide (DMSO), tetrahydrothiophene oxide (TPO), thioxane oxide (TSO) and thiacyclohexane oxide (TCHO). Among the amine oxides, pyridine-N-oxide (PYO) and its parasubstituted analogs seem most appropriate. In this report, we shall primarily discuss the complexes formed with TSO and TCHO. We shall mention additional complexes where appropriate, for other ligands give results in agreement with those obtained with the dipolar oxygen ligands mentioned above.

Choice of Anion. The best results for understanding of coordination numbers are obtained when a large, non-complexing, mononegative anion is used. We have employed perchlorate ion throughout this study, but it is not without faults. Chief among these is the

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[1] Taken in part from the Sc. B. theses of J. A. S. (1962) and R. J. G. (1964).
[2] R. L. Carlin, J. Roitman, M. Dankleff and J. O. Edwards, *Inorg. Chem.*, *1*, 182 (1962).
[3] J. O. Edwards and J. A. Stritar, *Science*, *142*, 3600 (1963).

explosive nature of metal perchlorate complexes with organic ligands. The anions BF_4^-, PF_6^-, and AsF_6^- would have some advantage, however we found it difficult to remove all fluoride ion which is a serious contaminant in most of our cases. Tetraphenylborate ion would be interesting as a non-complexing anion, however it would complicate the elemental analyses because of its large amount of carbon and hydrogen.

It is necessary to exclude complexing anions such as Cl^-, Br^-, I^- and SCN^-. These anions can have an effect on the coordination number of the cation to which they are bound. For example, only one or two dipolar oxygen ligands will unite with halide compounds of the zinc family, whereas the perchlorates generally combine with six dipolar oxygen ligands. Complexes with anions such as nitrate, acetate, and sulfate also have been found to give misleading results; the results with uranyl ion[3] clearly show this.

Results

Complexes. In Table I, data on some new complexes of thioxane oxide (TSO) and metal perchlorate are presented. Both transition metals and non-transition metals are included, and it appears that this ligand is not unlike other dipolar oygen ligands in forming stable characteristic complexes.

In Table II, data on some new complexes of thiacyclohexane oxide (TCHO) and metal perchlorates are presented. In Table III, five miscellaneous new compounds are presented.

The infrared spectra of TSO complexes were taken, and an assignment of the sulfur-oxygen stretching mode was made following the procedure of Cotton, Francis, and Horrocks.[4] The band so assigned is listed in Table IV. In all cases, but two to be discussed below, the band at 1020 cm^{-1} had moved to lower

Table I. Metal Perchlorate Complexes with Thioxane Oxide

		C, %		H, %		Cl, %		S, %	
	Color	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[Mn(TSO)_6](ClO_4)_2$	white	29.57	30.45	4.96	4.91	7.27	7.34	19.74	19.27
$[Fe(TSO)_6](ClO_4)_2$	pale yellow	29.54	29.44	4.96	5.19	7.27	7.26	19.72	19.30
$[Fe(TSO)_6](ClO_4)_3$	yellow	26.81	26.49	4.49	4.99	9.90	10.01	17.90	17.45
$[Co(TSO)_6](ClO_4)_2$	pink	29.45	29.49	4.99	5.50	7.25	7.26	19.65	19.58
$[Cu(TSO)_6](ClO_4)_2$	light blue[a]	29.28	29.25	4.93	4.99	7.21	7.55	19.58	19.41
$[Cu(TSO)_4](ClO_4)_2$	aqua[b]	25.86	24.74	4.34	4.43	9.54	9.51	17.26	16.11
$[Zn(TSO)_6](ClO_4)_2$	white	29.36	29.49	4.91	5.19	7.20	7.27	19.53	19.33
$[Cd(TSO)_6](ClO_4)_2$	white	27.93	28.35	4.67	4.78	6.87	6.74	18.65	19.41
$[Mg(TSO)_6](ClO_4)_2$	white	30.52	30.35	5.09	5.30	—	—	20.40	20.24
$[Ca(TSO)_6](ClO_4)_2$	white	30.03	30.22	5.04	5.08	7.37	7.38	20.04	19.82
$[Sr(TSO)_6](ClO_4)_2$	white	28.61	28.73	4.81	4.81	—	—	19.10	19.25
$[Ce(TSO)_9](ClO_4)_3$	white	28.44	28.31	4.78	4.75	7.00	7.05	18.99	18.42
$[Y(TSO)_9](ClO_4)_3$	white	29.44	29.43	4.94	5.24	—	—	19.56	19.32
$[Al(TSO)_6](ClO_4)_3$	white	27.55	24.90	4.62	5.07	10.17	10.26	18.39	17.63
$[In(TSO)_6](ClO_4)_3$	white	25.42	25.45	4.27	4.25	—	—	16.96	17.28
$[Sc(TSO)_6](ClO_4)_3$	white	27.08	27.37	4.55	4.54	9.99	9.93	—	—

[a] Cu, %: Calcd 6.46; Found 6.82. [b] Cu, %: Calcd 8.55; Found 8.56.

Table II. Metal Perchlorate Complexes with Thiacyclohexane Oxide

		C, %		H, %		S, %		Cl, %	
Compound	Color	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[Mg(TCHO)_6](ClO_4)_2$	white	38.63	38.46	6.49	6.41	20.63	20.48	7.60	7.06
$[Sr(TCHO)_6](ClO_4)_2$	white	36.42	36.15	6.07	6.09	19.31	16.63	7.13	7.59
$[Zn(TCHO)_6](ClO_4)_2$	white	37.32	37.11	6.21	6.16	19.79	20.08	7.29	7.31
$[Cd(TCHO)_6](ClO_4)_2$	white	35.60	35.17	5.93	5.73	18.85	18.60	6.95	7.04
$[Hg(TCHO)_6](ClO_4)_2$	white	32.80	32.60	5.46	5.42	17.38	17.76	6.40	6.15
$[La(TCHO)_9](ClO_4)_3$	white	36.22	36.09	6.04	5.81	19.24	18.98	7.10	7.35
$[In(TCHO)_6](ClO_4)_3$	white	32.28	32.48	5.38	5.49	17.12	17.27	9.49	9.62
$[Tl(TCHO)_6](ClO_4)_3$	white	29.71	29.15	4.99	4.76	15.90	15.76	8.79	8.95

Table III. Some other new Sulfoxide Compounds

		C, %		H, %		Other, %		
Compound	Color	Calcd.	Found	Calcd.	Found	Element	Calcd.	Found
$Th(NO_3)_4.4TSO$	white	20.00	19.84	3.36	3.24	N	5.83	6.00
$PdCl_2.2TSO$	orange	22.99	25.31	3.86	4.29	Cl Pd	16.97 25.53	16.16 24.21
$Cd(ClO_4)_2.5DMSO$	white	17.11	17.32	4.31	4.39	Cl S	10.10 22.84	10.22 21.30
$Cr(ClO_4)_3.5TSO.C_2H_5OH$	green	26.50	27.73	4.67	4.63	S Cl	16.08 9.81	15.98 10.14
$NaClO_4.2TSO$	white	26.50	27.12	4.45	4.69	S	17.75	18.61

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(4) F. A. Cotton, R. Francis and W. D. Horrocks Jr., *J. Phys. Chem.*, *64*, 1534 (1960).

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$Cr(ClO_4)_3.5TSO.C_2H_5OH$	green	26.50	27.73	4.67	4.63	S	16.08	15.98
$NaClO_4.2TSO$	white	26.50	27.12	4.45	4.69	Cl S	9.81 17.75	10.14 18.61

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(4) F. A. Cotton, R. Francis and W. D. Horrocks Jr., *J. Phys. Chem.*, 64, 1534 (1960).

Octahedral complexes with magnesium ion are expected, and the two compounds prepared agree. The complexes formed with strontium ion, and to a lesser extent with calcium ion, are surprising for a higher coordination number than six is probable; in solids wherein coordination numbers to oxygen have been determined by X-ray, higher coordination numbers (e.g., nine) have been reported. Also the data on trivalent cations such as the Lanthanides (see Below) indicate that a higher coordination number is to be expected for the alkaline earth metal cations. Further study of the interaction of the dipolar oxygen ligands with these cations seems to be required.

Trivalent Cations. Possibly the most interesting set of complexes are those formed by the trivalent metal perchlorates. Six coordination seems to be most probable for some of the cations, but several rare earth complexes with nine sulfoxide ligands have been prepared. It seems unlikely that size alone is the dominant factor here.

With small monodentate oxygen ligands, six is the expected coordination number for aluminum ion. Coordination with fluoride ion and with a variety of oxygen ligands is observed; examples are AlF_6^{3-} and $Al(H_2O)_6^{3+}$. These ions in octahedral configuration are known to exist in solids containing aluminum ion, as has been shown by X-ray studies. The species $Al(TSO)_6^{3+}$ and $Al(DMSO)_6^{3+}$ are most probably octahedral also. The coordination number for $Al_{(aq)}^{3+}$ has been reported to be six.[12]

The three post-transition trivalent cations Ga^{3+}, In^{3+} and Tl^{3+} all add six sulfoxide ligands as did the three post-transitions divalent cations Zn^{2+}, Cd^{2+} and Hg^{2+}. A *nmr* study[13] of the coordination number of Ga^{3+} indicates that six is the number in aqueous solution. It seems probable that all of these complexes involve six ligands in octahedral coordination, since such was found to be the case for mercuric ion.[2]

By way of contrast, the trivalent cations on the left hand side of the Periodic Chart are not limited to six coordination. Sc^{III} does add six TSO molecules, but the rare earth cations (Y^{3+}, La^{3+} and Ce^{3+}) add nine ligands. Also nonahydrates such as $Nd(BrO_3)_3.9H_2O$ has been observed, and it seems likely that all nine water molecules are in the coordination sphere. Morgan[13] has interpreted the proton relaxation data for gadolinium ion in aqueous solution as being consistent with either 8 or 9 as the coordination number with water as ligand. He also points out that not all Lanthanide ions necessarily will have the same number, and that it is possible for one cation to have more than one number. As in the case of the alkaline earth cations, further study seems required.

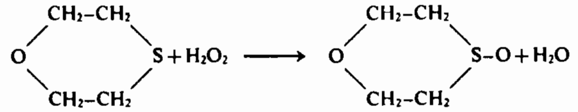
Conclusion

Certainly the most important conclusions from this study are that it is possible using properly-designed systems to synthesize coordination compounds of certain non-transition metal cations with monodentate oxygen ligands and that the stoichiometry of such complexes lead to predictions as to the nature of the hydrated cation in solution. The data on mercuric ion[2] and uranyl ion[3] clearly demonstrate the points. The new data presented in this report suggest that other cases, such as the coordination of thallic ion, will soon be clarified.

It would be naive to assume that the above mentioned method presents a conclusive answer to the problem of the coördination numbers of these metals with oxygen ligands. Indeed the development of satisfactory n.m.r. techniques has in some cases been quite definitive.[12,13] It appears safe to say that no single technique will be applicable to all cases and that the several methods should all be applied to those cases still unresolved. Some cations, such as Ag^+ and Pb^{2+}, have not given satisfactory coordination compounds as yet, but new ligands and new experimental methods may lead to a significant understanding of their aqueous coordination chemistry.

Experimental Section

Reagents. Commercial, 1,4-thioxane and an equimolar amount of hydrogen peroxide were refluxed in methanol for 15 hours. The methanol was then evaporated and most of the water formed by the reaction was removed by azeotropic distillation with benzene. The crude sulfoxide (TSO) was stored over barium oxide for 24 hours and distilled at reduced pressure; b.p. 136° at 14.5 mm.



Thiacyclohexane was prepared from commercially available 1,5-dibromopentane and Na_2S fused chips by the method of Haines.[15] The product was distilled at reduced pressure; b.p. 37° at 9 mm. It was then oxidized with 50% H_2O_2 (equimolar amounts) in acetone solution containing 5 ml. of p-toluene sulfonic acid (per 50 gm of thiocyclohexane) as catalyst. When the initial reaction had subsided, the solution was refluxed for thirty minutes. The solvent was stripped off with an aspirator; the liquid remaining was dried over $CaCl_2$ and distilled at reduced pressure; b.p. 123-124° at 15 mm. Thiacyclohexane oxide (TCHO) is a white solid which is extremely hygroscopic and is unstable at higher temperatures.

Commercial dimethyl sulfoxide (DMSO) was purified by distillation at reduced pressure from barium oxide.

The metal perchlorate were all obtained commercially except for those of La, Sr, and Y and Sc which were prepared from the oxides or the carbonates by neutralization with perchloric acid.

Other metal salts and solvents were reagent grade and were used without further purification.

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(12) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, 39, 1349 (1963).

(13) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, 88, 4754 (1966).

(14) L. O. Morgan, *J. Chem. Phys.*, 38, 2788 (1963).

(15) Haines, *J. Phys. Chem.*, 60, 549 (1956).

Complexes. The complexes, except where specifically noted below, were prepared by the addition of the appropriate metal salt in ethanol, methanol or acetone to a solution of excess sulfoxide (about 10: 1) in the same solvent. A small amount of perchloric acid was necessary to prevent hydrolysis in the cases of trivalent Y, In and Tl. Most of the complexes precipitated immediately, and others precipitated on cooling of the solution. In the case of $Cd(ClO_4)_2$ and DMSO, the addition of ether was necessary in order to obtain the solid. In the majority of cases the complexes could be recrystallized from methanol, although this was not always necessary. If their melting points allowed, the complexes were dried in vacuo at 65°.

$Cr(ClO_4)_3.5TSO.C_2H_5OH$. Hydrated chromium(III) perchlorate and TSO in 1: 10 molar ratio were dissolved in 50-50 ethanol-acetone and the solution heated to boiling. The purple solution gradually turned light green, and a green flocculent precipitate formed; this was filtered and washed with acetone. Purification was accomplished by boiling acetone and drying in vacuo at 65°. In the absence of ethanol, a green oil was obtained.

$PdCl_22TSO$. An aqueous solution of TSO and $PdCl_2$ (in 2: 1 molar ratio) was evaporated. A light-orange powder was formed and this was filtered and washed with water and acetone. Recrystallization from $CHCl_3$ yielded bright orange crystals which were filtered, washed with acetone, and dried in vacuo.

$Tl(ClO_4)_3.6TCHO$. Thallium(III) perchlorate was dissolved in methanol and 90% perchloric acid was added dropwise until the precipitate (presumably due to solvolysis) went into solution. A solution of TCHO in methanol was added and the compound precipitated upon cooling. The product was not recrystallized.

$In(ClO_4)_3.6TCHO$. The procedure used for the above case was employed, however the desired compound precipitated without the need of cooling and it could be recrystallized from a dilute solution of TCHO in methanol.

In several instances (*e.g.* thallium(I) perchlorate and TCHO) an intractable oil was obtained. Such cases are not reported herein.

Spectra. Infrared spectra in the region 2.5 to 15.0 microns were taken on a Perkin-Elmer Model 137 (Infracord) spectrophotometer calibrated with a polystyrene film. The solid samples were run in either KBr pellets or Nujol mulls.

Caution. The grinding of metal perchlorate complexes is dangerous as these compounds may detonate upon such treatment.

Analyses. The elemental analyses were carried out by Schwarzkopf Microanalytical Lab., Woodside, New York.

Acknowledgments. The authors are grateful to Professor R. L. Carlin and Mr. W. Henry for helpful discussion, and to the Advanced Research Projects Agency (Department of Defense) and the U.S. Atomic Energy Commission for financial support.