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Nickel Halide Complexes of Ethylene Glycol and Oxygen-Substituted Glycols

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Although solid complexes of ethylene glycol and nickel salts were isolated 60 years ago,[1] little is known of their coordination chemistry. A recent report on related compounds suggests they are useful synthetic intermediates.[2] We have undertaken an examination of ethylene glycol and its O-alkyl-substituted derivatives to elucidate their coordination properties. Evaluations are made in light of reaction products formed with nickel halide salts.

30,000 cm^{-1}) were measured with a Cary Model 14 spectrophotometer. A modified technique of Griswold[3] was employed in which Fluorolube mulls were painted on filter paper strips and then immersed in optical cells containing Fluorolube. The reference cell utilized a filter paper blank in Fluorolube.

Results and Discussion

Bis complexes were obtained for both nickel chloride and nickel bromide with the ligands ethylene glycol (glycol), 2-methoxyethanol (Me-gly), and 2-ethoxyethanol (Et-gly). Of these three ligands, only 2-ethoxyethanol formed an isolable bis product with nickel iodide. 1,2-Dimethoxyethane (glyme) formed mono complexes with nickel chloride and bromide but a bis compound with nickel iodide. Our attempts to duplicate the reported preparation[4] for bis(glyme)–NiBr$_2$ always resulted in the mono complex. Ligand abbreviations are given in parentheses. Solid products of constant composition could not be prepared from 1,2-diethoxyethane and any halide salt. No tris com-

TABLE I
ANALYTICAL INFORMATION FOR ISOLATED COMPLEXES

Compound[a]	Prepn	Color	% C Calcd	% C Found	% H Calcd	% H Found	% Ni Calcd	% Ni Found
Ni(glycol)$_2$Cl$_2$	1	Green	18.94	19.13	4.77	4.73	23.14	22.87
Ni(glycol)$_2$Br$_2$	1	Yellow	14.02	13.87	3.53	3.58	17.13	17.35
Ni(Me-gly)$_2$Cl$_2$	1	Yellow	25.57	25.70	5.72	5.70	20.83	20.80
Ni(Me-gly)$_2$Br$_2$	1	Yellow	19.44	19.37	4.35	4.16	15.84	15.60
Ni(Et-gly)$_2$Cl$_2$	2	Yellow	31.01	30.75	6.51	6.53	18.95	19.28
Ni(Et-gly)$_2$Br$_2$	1	Yellow	24.09	23.70	5.17	4.96	14.72	14.66
Ni(Et-gly)$_2$I$_2$	2	Tan	19.50	19.20	4.09	3.96	11.91	12.18
Ni(glyme)Cl$_2$	4	Tan	21.86	21.52	4.59	4.71	26.72	26.79
Ni(glyme)Br$_2$	3	Brown	15.57	15.70	3.27	3.49	19.02	18.77
Ni(glyme)$_2$I$_2$	3	Red	19.50	19.50	4.09	3.97	11.91	11.88

[a] Glycol = C$_2$H$_6$O$_2$; Me-gly = C$_3$H$_8$O$_2$; Et-gly = C$_4$H$_{10}$O$_2$ = glyme.

Experimental Section

Materials.—Anhydrous nickel salts were used in all preparations. Ligands were refluxed over desiccants and distilled in a dry atmosphere immediately before their use. Their infrared spectra indicate the absence of water.

Preparations.—The following methods were used as specified in Table I: 1, solid products formed on cooling a refluxed nickel halide–ligand solution; 2, solid products precipitated on addition of ether to a nickel halide–ligand solution; 3, extraction of finely powdered halide salt with ligand formed a solution from which solid products developed; 4, concentration under vacuum of a saturated nickel halide–methanol solution to which ligand had been added resulted in a syrup. Solid product separated on addition of ether, and was suspended in warm ligand before final separation. All solids were isolated by filtration and dried in a dry air stream, after washing with methanol–ether (glycol), ligand (NiI$_2$–glyme), or ether.

Measurements.—Nickel was estimated as dimethylglyoximate in the usual manner, and C–H analyses were determined in our laboratory using a Coleman Model 30 analyzer in conjunction with a Mettler M5 microbalance.

Room-temperature magnetic susceptibilities were measured at two field currents by the Gouy method in the standard manner. Diamagnetic corrections were applied.

A Perkin-Elmer 457 grating spectrophotometer recorded vibrational spectra (4000–250 cm^{-1}) with samples as Nujol and Fluorolube mulls. Spectra of purified ligands were determined neat and also as chloroform solutions. Electronic spectra (6000–

plexes were isolated. The complexes are unstable in air, and solution was accompanied by decompositionl Formulas, colors, preparative method, and analytica. information for the products are listed in Table I.

In the infrared spectral region above 2800 cm^{-1} complexes display broad and intense bands attributed to O–H and C–H stretching modes. Compared to free ligands, bands assigned as O–H appear at lower energies (350–550 cm^{-1}) in the complex. The decrease depends on the halide ion present, being greatest for chloride ion. All ligands and complexes also exhibited sharp intense absorption bands between 1150 and 1000 cm^{-1} due to C–O stretching. Bands for the complex again appear at lower energies, relative to free ligand. These changes are more pronounced for ligands with one OH group, *i.e.*, Me- and Et-gly, than for glycol or glyme.

All bis-ligand complexes have moments (3.30 ± 0.05 BM) considered normal for pseudooctahedral nickel-(II), whereas mono-ligand complexes have higher values (3.50 ± 0.05 BM). Spin–orbit coupling constants estimated from both magnetic and spectroscopic[5] data are larger for mono complexes and suggest that a greater orbital contribution is present here.

(1) A. Grün and E. Boedecker, *Ber.*, **43**, 1051 (1910).
(2) L. G. L. Ward, D. P. Jordan, and D. H. Antonsen, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 27.

(3) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1279 (1964).
(4) H. P. Schröer and B. Heyn, *Z. Chem.*, **7**, 238 (1967).
(5) J. Reedijk, P. W. N. M. van Leeuwen, and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, **87**, 129 (1968).

Electronic spectra for samples in oil mulls consist of three main absorption areas. Assignments are based on an O_h coordination model because of absorption energies,[6] spectral display, and magnetic moments. The split middle band (ν_2) is typical of those dealt with by van Leeuwen.[5] Its calculated[7] energy ($^3A_{2g} \rightarrow {}^3T_{1g}$ (F)) was always within the observed range. Based on analytical, magnetic, and spectral evidence, these complexes are pseudo-O_h weak-field cases. Other properties imply they are coordination polymers. Observed and calculated d–d bands, β values, and magnetic moments are listed in Table II.

TABLE II
d–d SPECTRA (kK) AND MAGNETIC MOMENTS FOR
SOLID COMPLEXES

Compound	ν_1	ν_2		ν_3	β	Calcd ν_2	μ_{eff}. BM
Ni(glycol)$_2$Cl$_2$	8.22	12.9	14.2	23.9	0.79	13.6	3.36
Ni(glycol)$_2$Br$_2$	8.12	12.7	13.8	23.5	0.77	13.4	3.25
Ni(Me-gly)$_2$Cl$_2$	7.70	12.7	14.1	23.5	0.82	12.9	3.29
Ni(Me-gly)$_2$Br$_2$	7.78	12.5	13.7	23.3	0.80	13.0	3.36
Ni(Et-gly)$_2$Cl$_2$	7.65	12.5	14.1	23.4	0.81	12.8	3.35
Ni(Et-gly)$_2$Br$_2$	7.47	12.5	13.9	23.0	0.81	12.5	3.32
Ni(Et-gly)$_2$I$_2$	7.43	12.1	13.3	...[a]	...	...	3.33
Ni(glyme)Cl$_2$	6.91	11.6	13.2	22.0	0.80	11.6	3.54
Ni(glyme)Br$_2$	6.70	11.1	12.3	21.2	0.76	11.3	3.46
Ni(glyme)$_2$I$_2$	6.90	11.6		...	...	...	3.27

[a] Unlisted bands are masked by charge-transfer absorptions.

Evidence of extensive band splitting is lacking, indicating a uniform average field. Thus average environment calculations were used to approximate ligand Dq values. For bis complexes a NiO$_4$X$_2$ format resulted in regular Dq decreases with O-alkyl substitution and gave most reasonable magnitudes of Dq. Conversely, monoglyme compounds are more agreeable

(6) B. N. Figgis, "Introduction to Ligand Fields." Interscience, New York, N. Y., 1966, p 220.
(7) A. B. P. Lever, *J. Chem. Educ.*, **45**, 711 (1968).

with a NiO$_2$X$_4$ coordination type involving bridging halide ions. Both models imply bonding two oxygen atoms per ligand, as in other similar systems.[8–11] A spectrochemical series of glycol (890) > 2-methoxyethanol (860) > 2-ethoxyethanol (810) > glyme ($\sim$750) is obtained from average field calculations. We have isolated tris complexes of glycol and 2-methoxyethanol for a companion study and obtain Dq values of 887 and 868 cm^{-1} from their mull spectra. These independent results support our calculations well.

Our work substantiates previous measurements from 2-methoxyethanol solutions of nickel bromide[12] and identifies a reported uv–visible spectrum[13] as that of tris(glycol)nickel(II). Pronounced reduction in coordinating ability by O-alkyl substitution is demonstrated by this series. Similar changes for N-alkyl-substituted ethylenediamines[14] are not as extensive in curtailing coordination. Although glycol is slightly better than water as a ligand, remaining members are weaker. This ligand system is comparable to urea, THF, DMSO, substituted and cyclic amides, thiourea, and substituted pyridine N-oxides in terms of donor strengths.

(8) R. J. H. Clark and W. Errington, *Inorg. Chem.*, **5**, 650 (1966).
(9) G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *J. Chem. Soc.*, 5873 (1963).
(10) G. W. A. Fowles, P. T. Greene, and T. E. Lester, *J. Inorg. Nucl. Chem.*, **29**, 2365 (1967).
(11) G. W. A. Fowles and T. E. Lester, *ibid.*, **31**, 657 (1969).
(12) D. A. Fine, *Inorg. Chem.*, **5**, 197 (1966).
(13) N. S. Chhonkar, *J. Chem. Phys.*, **41**, 3683 (1964).
(14) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965).

Correspondence

Bonding by Outer d Orbitals and by Continuum Orbitals in Molecules of Second-Row Atoms

Sir:

Recently Jørgensen[1,2] has made the interesting suggestion that the acceptor properties of the PF$_3$ group in complexes of transition metals in low oxidation states, for example, Fe(PF$_3$)$_5$ and Co(PF$_3$)$_4$I, can be understood in terms of the involvement in bonding of continuum orbitals. Additionally, Jørgensen suggested that the involvement in bonding by 3d orbitals at phosphorus is very small, and *prima facie* this contrasts with the viewpoint that ascribes the acceptor properties of PF$_3$ in complexes to the availability of

(1) C. K. Jørgensen, *Chimia*, **23**, 292 (1969).
(2) C. K. Jørgensen, *Struct. Bonding* (Berlin), **3**, 106 (1967).

the 3d orbitals at phosphorus.[3] The purpose of this letter is to discuss Jørgensen's proposal in relation to the conventional models of bonding based on the overlapping of discrete orbitals of either atomic or molecular character.

In principle, even molecules of phosphorus and sulfur in high coordination states can be accommodated in bonding schemes which neglect 3d orbitals altogether,[4] although recent support for the concept of bonding by 3d orbitals[5] is suggested by the calculations of Boer, Boyd, and Lipscomb[6–8] which use minimum basis sets of

(3) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966.
(4) R. E. Rundle, *Surv. Progr. Chem.*, **1**, 81 (1963); J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).
(5) C. A. Coulson, *Nature* (London), **221**, 1106 (1969); K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).
(6) D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967).
(7) D. B. Boyd and W. N. Lipscomb, *ibid.*, **48**, 4968 (1968).
(8) F. P. Boer and W. N. Lipscomb, *ibid.*, **50**, 989 (1969).