CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA

Expanded Ring Metal Complexes of *o*-Xylylenediamine and Homo-*o*-xylylenediamine

BY ROBERT C. BRASTED, THOMAS D. O'BRIEN, AND WALDEN L. HEINO

Received August 26, 1963

Ring complexes of seven and eight members have been formed and isolated from methanol as a reaction medium using diamine chelating agents whose donor sites have been sterically directed. The concentration and thermodynamic dissociation constants of the dihydrochlorides of two ligands used in this study, *o*-xylylenediamine and homo-*o*-xylylenediamine (abbreviated as oxyn and hoxyn, respectively), are reported for the first time. The existence of both a di- and a trinuclear complex for the copper–oxyn complex, $[Cu_2(oxyn)_6](ClO_4)_4$ and $[Cu_3(oxyn)_8](ClO_4)_6$, is reasonable from color, melting point, solubility, and gravimetric analytical data. Structures are suggested for these two species in which copper exhibits both the five and six coordinate states. In addition to the copper–oxyn system, others isolated from methanol are: $[Cu(hoxyn)_2](ClO_4)_2$, $[Ni(oxyn)_3](ClO_4)_2$, $[Zn(oxyn)_2](ClO_4)_2$, and $[Zn(hoxyn)_2](ClO_4)_2$. Each of these complexes decomposes in water to form the metal hydroxide. The relative susceptibility of hydroxide attack on the metal ion of the complex has been found to follow generally the Irving–Williams stability series.

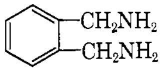
Introduction

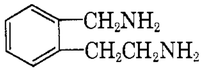
The relationship between the stability of chelate rings and the number of atoms in the ring has been extensively studied and has been reviewed elsewhere.[1,2] In general, for rings containing a single metal atom and a diamine chelating agent of the general formula $NH_2(CH_2)_nNH_2$, there is evidence that ring stability is maximum for $n = 2$ (assuming saturated systems), decreases to a minimum for $n = 5$ or 6, and finally increases as the ring size (including the metal atom) reaches nine. There is reasonable doubt as to whether ring closure actually takes place with bidentate chelating agents of such size and weight. It is possible that polynuclear species may form or that the ligand may function as monodentate with water molecules occupying some of the normal coordination sites of the metal atom. It is, in fact, difficult to differentiate experimentally between ring closure and bridging for amines with values of n above 3. The nucleophilicity of such amines is sufficiently great to favor the formation of metal hydroxides in aqueous solution over that of an amine complex.

The feasibility of sterically directing donor atoms of a bidentate ligand to increase the probability of ring closure is suggested by a fairly large body of data in the literature. Chelation to form an eight-membered ring does not occur with $S(CH_2COO)_2^{-2}$, but does when the acetato groups are directed through conversion of the sulfur to a sulfone group, $O_2S(CH_2COO)_2^{-2}$.[3] Homophthalic acid, $C_6H_4(COO)(CH_2COO)^{-2}$, forms an eight-membered ring with cobalt(III), whereas only polymeric species of unknown composition result when this metal is added to straight chain dicarboxylates.[4] Dicarboxylate ethyl esters of oxalic, malonic, and glutaric acids have been used as bidentate chelating agents to form complexes with titanium(IV), tin(IV), and zirconium(IV) chlorides. For each ligand the stability order was Ti < Sn < **Zr**.[5]

The two ligands 1,2-diaminocyclohexane-N,N-tetraacetic acid and ethylenediaminetetraacetic acid form complexes of different stabilities with Ca, Mg, Ba, and Hg(II). The geometry of the former ligand with a *cis* carbon structure of the ring appears to be of importance in forming the more stable species. Again, the calcium complex of 1,5-dicarboxypyridine is more stable than that of diacetatoamine, $[HN(CH_2COO)_2]^{-2}$. Both ligands form eight-membered rings, but the donor sites of the former chelating agent are more favorably arranged for coordination than are those of the latter.[6–8]

In the current study two ligands containing an aromatic ring as part of the carbon framework between donor atoms have been synthesized. These are


o-xylylenediamine (oxyn)


homo-*o*-xylylenediamine (hoxyn)

These ligands provide a ready means for investigation of the steric and electronic effects resulting from insertion of an aromatic ring in the carbon framework of the bidentate ligand. Metal ions which appear to participate in ring closure with these ligands were copper(II), zinc(II), nickel(II), and cobalt(II).

Experimental

Preparation of Amines. *o*-Xylylenediamine Dihydrochloride.—The Gabriel phthalimide synthesis was used with the terminal acid hydrolysis step being accomplished by a sealed-tube process in preference to a reflux with hydrochloric acid or the hydrazine

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[4] J. Duff, *ibid.*, **119**, 1982 (1921).

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[6] G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

[7] G. Schwarzenbach and H. A. Ackermann, *ibid.*, **32**, 1682 (1949).

[8] G. Schwarzenbach and R. Bauer, *ibid.*, **39**, 722 (1956).

hydrate reflux process of Ing and Manske followed by HCl treatment. The sealed tube process gave superior yields.[9-12]

Homo-*o*-xylylenediamine Dihydrochloride.—This ligand was obtained by the Curtius rearrangement of *o*-phenyleneaceticpropionic acid dihydrazide. The acid hydrolysis step of the intermediate diurethane was accomplished by prolonged refluxing (50 hr.) with HCl, replenishing the HCl supply from time to time.[13,14]

Anal. Calcd. for *o*-xylylenediamine dihydrochloride $C_8H_{14}N_2Cl_2\cdot 0.5H_2O$: C, 44.05; H, 6.93; N, 12.85. Found: C, 44.80; H, 6.90; N, 12.27.

Anal. Calcd. for homo-*o*-xylylenediamine dihydrochloride, $C_9H_{16}N_2Cl_2$: C, 48.44; H, 7.23; N, 12.56. Found: C, 49.10; H, 7.37; N, 12.29.

The acid dissociation constants for these diamines were determined by the usual base titration procedures of Bjerrum and are here reported for the first time.[15,16] The essential information derived from these titrations is included in Table I. Data on ethylenediamine are included for comparison. The terms c_0 and b_0 represent the initial concentrations of the acid (diamine dihydrochlorides) and the base (sodium hydroxide), respectively. The volumes B_1, EP_1, B_2, and EP_2 represent the acid being one-fourth neutralized, the first end point, three-fourths neutralized, and the second end point, respectively. The pH values at these points are noted. Activity coefficients, necessary for the estimation of the thermodynamic constants, $\text{p}K_1^0$ and $\text{p}K_2^0$, were determined from the plots of the volume ionic strength, μ, against the molar activity coefficients, γ, for the H^+, oxynH, hoxynH, enH, oxynH_2, hoxynH_2, and enH_2.[17]

Table I

Titration Data on Diamines

	Ethylenediamine dihydrochloride	*o*-Xylylenediamine dihydrochloride	Homo-*o*-xylenediamine dihydrochloride
c_0, M	0.0120	0.0120	0.0120
b_0, M	0.0605	0.0605	0.0604
B_1, ml.	4.96	4.96	4.96
	(pH 6.88)	(pH 7.53)	(pH 8.38)
EP_1, ml.	9.92	9.92	9.93
	(pH 8.94)	(pH 8.74)	(pH 9.13)
B_2, ml.	14.88	14.88	14.88
	(pH 9.85)	(pH 9.92)	(pH 9.89)
$\text{p}k_1$	6.93 ± 0.06	7.48 ± 0.04	8.37 ± 0.06
$\text{p}k_2$	9.81 ± 0.06	9.88 ± 0.05	9.81 ± 0.07
$\text{p}K_1^0$	6.80 ± 0.06	7.35 ± 0.04	8.24 ± 0.06
$\text{p}K_2^0$	9.80 ± 0.06	9.87 ± 0.05	9.81 ± 0.07

Titrations in Aqueous Solution.—Potentiometric titrations of the dihydrochlorides of oxyn and hoxyn with standard base in the presence of the metal ions Cu(II), Ni(II), Co(II), Co(III), and Zn(II) were carried out using essentially the same techniques as for the determination of the acid dissociation constants.[15,16] A displacement of the curve of pH against the ml. of sodium hydroxide added toward lower pH values (ΔpH) is considered to be evidence for the formation of an amine complex, with the magnitude of this difference being an indication of the stability of the complex. Although there were slight displacements in each of the metal ion titration curves, there was an accompanying precipitation of the metal hydroxide. Color changes for the Cu(II)–oxyn system coupled with the relatively slow appearance of copper(II) hydroxide were favorable evidence for complex formation in aqueous solution. An attempt to obtain stability data on the system from polarographic determinations was unsuccessful due to this hydroxide formation. With Ni(II)–oxyn a greenish solution resulted followed by precipitation. With Ni(II) and hoxyn only a flocculent precipitate formed with a colorless solution. The titration data for Zn(II)–oxyn suggested a complex more stable than that of Zn(II)–en. As for all systems, ethylenediamine–metal ion titrations were carried out for comparison purposes. That such was not the case was evident from the formation of $Zn(OH)_2$ before the stoichiometric end point and also from the fact that the shape of the curve could be attributed to the formation of a zincate species. For Co(II)–oxyn a color change from pink to blue was noticeable. With Co(II)–hoxyn a heavy blue-green floc was present before the stoichiometric end point with the supernatant liquid being colorless. Efforts to oxidize cobalt(II) to cobalt(III) by oxygen and peroxide in the presence of the diamines lead only to brownish mixed cobalt(II)-(III) oxide.

It was evident that in aqueous solution hoxyn was less effective than oxyn in forming complex species with the metal ions chosen and that neither diamine formed a complex more stable than the corresponding metal hydroxide.

Using the volume of NaOH added to the metal–ligand solution necessary to give a metal hydroxide precipitate as an indication of complex stability, it was found that the stability order for both ligands was Co < Ni < Cu > Zn. Such an order would follow from the Irving–Williams series.[18]

Preparation of Diamine Complexes Using Methanol as a Reaction Medium.—The procedure followed for the preparation of all complexes was essentially the same. The diamine hydrochloride (0.6 mmole) was placed in 8 M sodium hydroxide and the diamine extracted with ether. The ethereal solution was evaporated, the diamine taken up in methanol, and the metal solution added using an apparatus which permitted the multiple operations to be carried out without exposure to the atmosphere and moisture. Concentration and cooling of the metal–diamine solution afforded precipitation of the solid product. The latter was centrifuged, washed with methanol, and recrystallized. The solid product was again washed with methanol and ether and finally dried in air while being contained in the assembly. The amount of metal perchlorate solution (0.05 M) used in the reaction was determined from the stoichiometry represented by: $M + xA \rightleftarrows MA_x$, where x represents the usual coordination number of the metal ion and varies whether the amine is to function as a monodentate or a bidentate ligand. Two preparations for each complex were carried out, one with a 50% excess over that needed to form the ammine (monodentate) complex and the second assuming bidentate action of the ligand (with 50% excess) and that the maximum coordination number of the metal ion is assumed. In most cases simple evaporation was sufficient to give a precipitate of the complex. Copper complexes were less amenable to solid formation. Cooling at Dry Ice–acetone temperatures accompanied by buzzer agitation was needed. The metal perchlorates were prepared by addition of dilute perchloric acid to the metal oxide or carbonate. Vacuum drying gave the anhydrous salts.

With copper(II) perchlorate and oxyn, blue prismatic (twinned) crystals formed. The melting range was 128–136° with decomposition at 180°. The crystals were soluble in cold water but decomposed in a very short period of time giving black copper oxide. The blue crystals were obtained whether the first or second procedure was followed, that is assuming monodentate or bidentate coordination of the ligand.

Anal. Calcd. for $[Cu(oxyn)_3](ClO_4)_4$ or $[Cu_2(oxyn)_6](ClO_4)_4$: C, 42.96; H, 5.41; N, 12.53; Cu, 9.47. Calcd. for $[Cu_3(oxyn)_8](ClO_4)_6$: C, 40.95; H, 5.16; N, 11.94; Cu, 10.16. Found: C, 41.44; H, 5.97; N, 11.68; Cu, 10.2.

The analyses discount the existence of a tetracovalent Cu–oxyn (monodentate oxyn behavior) species. The possibility that the solid is polynuclear is excellent since the calculated analysis for the trinuclear is closer to the "found" data than that for a tris mononuclear species. As is so often the case for complexes of low stability in water and insolubility in suitable solvents for mo-

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[9] Beilstein, 13 H, p. 179.

[10] H. Strassman, *Ber.*, **21**, 576 (1888).

[11] S. Gabriel and G. Pinkus, *ibid.*, **26**, 2210 (1893).

[12] H. Ing and H. Manske, *J. Chem. Soc.*, 203 (1952).

[13] Beilstein, 13 E II, p. 166.

[14] L. Helfer, *Helv. Chim. Acta*, **6**, 790 (1923).

[15] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[16] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).

[17] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

[18] H. Irving and R. Williams, *J. Chem. Soc.*, 3192 (1953).

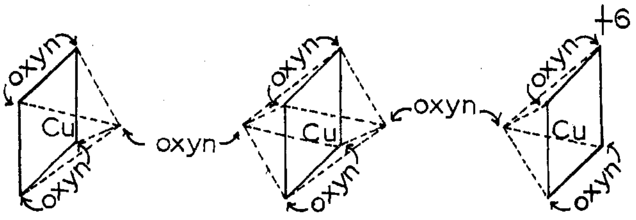

Fig. 1.—Proposed structure of $[Cu_3(oxyn)_8]^{+4}$ ion.

lecular weight determinations, the latter data were inconclusive. The broad melting range of the isolated blue solid would also strengthen the case of polynuclear form(s). Pfeiffer has reported a deep blue complex of copper(II) with hexamethylenediamine in methanol as a reaction medium. His analyses show a 1:3 ratio of metal to ligand.[19]

The present authors suggest two configurations (Fig. 1 and 2) describing a trinuclear and dinuclear complex, respectively. Coordination numbers of five and six are assumed for the copper(II) ion. It is doubtful that tetracovalent copper is as common as is often supposed. The square pyramid and octahedral combination in the trinuclear form seem more logical according to Gillespie's treatment of the five-coordinate state for transition metal ions (other than d^0 and d^{10}) than does an allowable (for a d^9 atom) combination of an octahedron with two trigonal bipyramids. The latter would involve $sp^3d_{x^2-y^2}$ orbitals.[20]

The copper(II) ion with hoxyn gave blue-violet massive prismatic crystals when a 1:2 ratio of Cu:hoxyn was used. It was necessary to use strong cooling (Dry Ice–acetone temperature) and dilution with ether to form the solid. Melting occurred at 184° with the formation of an orange liquid which charred at 240°. The aqueous solution appeared to be more stable to metal hydroxide formation than the Cu–oxyn system. With slight heating decomposition occurred. Analytical data are favorable to the formation of a bis chelate, $[Cu(hoxyn)_2](ClO_4)_2$. A dinuclear structure would not be unreasonable either as two octahedra joined at an edge or less plausibly two square planes bridged by hoxyn molecules.

Anal. Calcd. for $[Cu(hoxyn)_2](ClO_4)_2$: C, 38.41; H, 5.01; N, 9.96; Cu, 11.29. Found: C, 38.69; H, 5.21; N, 9.34; Cu, 11.3.

A reference previously was made to the zinc and oxyn system as giving positive results for complex formation in the potentiometric study in aqueous solution. From methanol, colorless prismatic tablets were isolated which aged to a well-developed massive form. The crystals were moderately soluble in methanol. At 238° they darkened and melted with swelling at 277–283°. The analyses were the same on crystals isolated from a large excess of the ligand.

Anal. Calcd. for $[Zn(oxyn)_2](ClO_4)_2$: C, 35.81; H, 4.51; N, 10.44; Zn, 12.18. Found: C, 35.20; H, 4.69; N, 10.35; Zn, 12.1.

The compound formed from zinc and hoxyn was not a well-defined crystalline species. The solid was in the form of white poorly formed platelets which did not improve in body with aging. The analyses, however, were the same regardless of the amount of hoxyn used, above that needed for a bis complex.

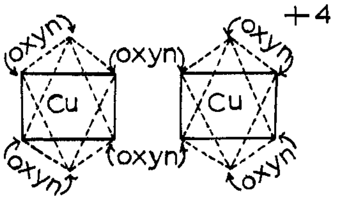

Fig. 2.—Proposed structure of $[Cu_2(oxyn)_6]^{+4}$ ion.

Anal. Calcd. for $[Zn(hoxyn)_2](ClO_4)_2$: C, 38.28; H, 5.00; N, 9.92; Zn, 11.58. Found: C, 37.91; H, 5.42; N, 8.96; Zn, 11.8.

Discussion and Summary

Ring closure in the formation of large ring complexes has been facilitated for a number of transition metal ions (Cu^{+2}, Zn^{+2}, Ni^{+2}, and Co^{+2}) by sterically directing the donor sites of ligands with some degree of unsaturation. The complexes of *o*-xylylenediamine and homo-*o*-xylylenediamine are unstable in water but stable in methanol. This solvent appears to be ideal as a preparative medium. The expected increase in stability in aqueous solution arising from the resonating double bond system in the ligands used over that in a simple polymethylenediamine did not occur. The general stabilities of metal complexes are comparable to those expected for tetra- and pentamethylenediamine chelates. The order of aqueous stability of both the oxyn and hoxyn complexes appears to follow generally the Irving–Williams series.

Complexes with seven and eight membered rings were formed using anhydrous transition metal perchlorates in methanol with *o*-xylylenediamine and homo-*o*-xylylenediamine, respectively. The acid dissociation constants of the dihydrochlorides of each of these diamines were determined and are herein reported. It is suggested that the complex with copper and oxyn is polymeric. Structures for dinuclear and trinuclear configurations are proposed in which coordination numbers of copper of five and six exist. Hoxyn gives complexes with copper and zinc with the latter being less well formed in the solid state than is the corresponding oxyn complex. Cobalt(II) does not give a complex with either oxyn or hoxyn, possibly due to the existence of water in the metal salts used as starting material. The product was contaminated with basic material. Cobalt(III) gives viscous and sirupy products with oxyn and hoxyn in methanol as well as water.

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[19] P. Pfeiffer, A. Bohm, and E. Schmitz, *Naturwissenschaften*, **35**, 190 (1948).

[20] R. J. Gillespie, *J. Chem. Soc.*, 4697 (1963).