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Potential Electron Transfer Complexes of the [M–O_4] Type: Synthesis and Properties of Complexes Derived from Pyrocatechol and Tetrachloropyrocatechol

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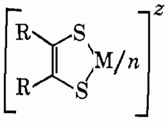
The existence of the electron-transfer series of general type $[M–O_4]^z$ has been thoroughly investigated using pyrocatechol and tetrachloropyrocatechol as ligands. Considering the normal oxidation state of metals such as Ni, Cu, and Zn and the stages of ligand oxidation, it is concluded that a five-membered series ($z = -2, -1, 0, +1, +2$) might exist in which the terminal members could be formulated as M(II) plus two ligand dianions ($z = -2$) and M(II) plus two *o*-quinones ($z = +2$). A search has been made for each member of this series using principally M = Ni. Detailed preparation and physical properties of dianionic complexes with M = Mg, Co, Ni, Cu, Zn, and Cd are given. Chemical and electrochemical oxidations of these dianions in conjunction with esr studies of the oxidation products gave no unambiguous evidence for the existence of monoanions related to those known in the $[M–S_4]^z$ series. However, the Ni and Cu dianions do undergo apparent one-electron electrochemical oxidations in dichloromethane solution. Materials with composition approximating that expected for the $z = 0$ members with M = Ni and Zn were isolated. The insolubility of these substances together with the paramagnetism of the nickel compounds suggests a polymerized structure. No evidence supporting the general existence of $z = +1$ species was found. Published results on the reactions of metal halides with *o*-quinones are cited to support the existence of the $z = +2$ unit, although the metal is undoubtedly also coordinated to halide in most cases. Electrochemical evidence is cited to indicate the probable existence of four members of a potential eight-membered electron-transfer series of general type $[Fe–O_6]^z$. A practical method for polarographic measurements using dichloromethane as a solvent is described.

Introduction

Following the initial demonstration[2] of the interrelationship of the complexes **1** by chemical and electrochemical one-electron-transfer reactions, a large number of such complexes have been characterized. Restricting present discussion to bis complexes ($n = 2$), the most novel and intriguing feature of their chemistry is the existence of one-electron-transfer reactions which have been utilized in the isolation of many species with M = Fe, Co, Ni, Pd, Pt, Cu, and Au, $z = 0, -1, -2$, and R = CN,[3] CF_3,[3a,4] aryl and alkyl,[5] and H.[6] In addition, complexes of type **2**, derived from toluene-3,4-dithiol having $z = -2, -1, 0$ have been detected polarographically for some metals and a number of complexes isolated.[7]



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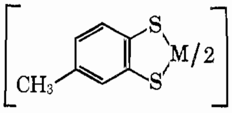

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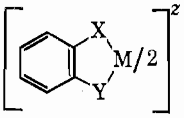
A highly significant question which arises at this point relates to the scope of electron-transfer reactions of four-coordinate complexes, inasmuch as at the outset of this investigation these reactions had been recognized only in the sulfur-bonded systems, especially **1**. We have been investigating the effect of changes in the donor atoms on the oxidation–reduction propensity of the general complex system **3**. On the basis of preliminary results already reported,[8] it is evident that electron-transfer series with X = Y = O; X = Y = NH; X = O, Y = S; X = S, Y = NH, and, principally, M = Ni exist, and that the half-wave potentials for a given oxidation–reduction step are strongly dependent upon the nature of X and Y. Our complete study of the complexes **3** with X = Y = O is presented here.



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We define the *complete* electron-transfer series for the complexes represented as $[M–O_4]^z$ to consist of the five members **4**–**8**. It is useful to formulate the most reduced member **4** as a complex of M(II) and the dianion of pyrocatechol (*o*-dihydroxybenzene), and the most oxidized member **8** as a complex of M(II) and an *o*-quinone. In this way the terminal oxidation states

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(1) (a) National Science Foundation Predoctoral Fellow, 1963–1966; (b) Alfred P. Sloan Foundation Fellow.

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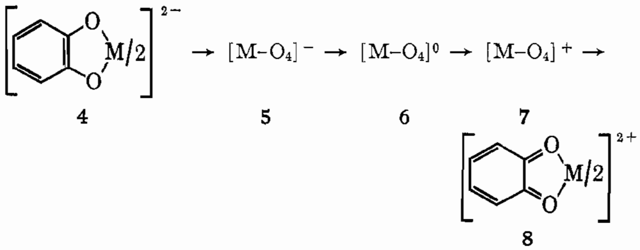
(8) A. L. Balch, F. Röhrscheid, and R. H. Holm, *ibid.*, **87**, 2301 (1965).



of the ligand system define the potentially stable limits of the electron-transfer series because there is little evidence that ligands with oxygen donors are effective in stabilizing unusually high or low oxidation states of a coordinated metal of the first transition series.[9] Formulations of the intermediate members **5**, **6**, and **7** are less useful and, in the absence of experimental evidence relating to electronic structures, possibly misleading. However, it should be noted the coordination of the semiquinone is a formal possibility.

In addition to the question of general significance raised above, several other motivating factors prompted our investigation of the potential electron-transfer series **4–8**. First, this ligand system is one of the very few in which distinct stages of oxidation—in this case dianion, semiquinone, quinone—are well recognized and the terminal reduced[10] and oxidized[11] members isolated. This statement is also true for numerous substituted variants of simple pyrocatechol. Second, unrelated reports already existing in the literature lend credence to the existence of members of the series **4–8**, although not necessarily involving the same ligand system or metal at each stage of oxidation. There are numerous reports of apparent bis(pyrocatecholato) complexes **4** with M = Co,[12–14] Ni,[13–15] Cu,[16] Zn,[15,17] and Cd,[15] the metals studied in the present investigation. Many of the crystalline solids were given unusual, if not bizarre, formulations based on elemental analyses. Among the relatively well-defined substances are pink $(NH_4)_2[Co(C_6H_4O_2)_2]$,[12,14] green $Na_2[Ni(C_6H_4O_2)_2]\cdot 12H_2O$,[13,14] olive-green $M^I_2[Cu(C_6H_4O_2)_2]$ with different cations and different content of water of crystallization,[16] white $(NH_4)_2[Zn(C_6H_4O_2)_2]$,[15] and pink $(C_5H_5N)_2[Cd(OC_6H_4OH)_2]$,[15] which should probably be reformulated as $(C_5H_5NH)_2[Cd(C_6H_4O_2)_2]$. Bu'Lock and Harley-Mason[18] report that the oxidation of catechol with persulfate in the presence of Zn^{2+} yields a greenish black solid which was not analytically well defined, but which is presumably $[Zn(C_6H_4O_2)_2]^0$, the intermediate member **6**. Apparently similar incompletely defined neutral complexes of barium with acenaphthenesemiquinone and indanesemidione, both blue-black in color, have been reported.[19] Finally, complexes of *o*-quinones (Q) such as 9,10-phenanthroquinone (but not *o*-benzoquinone) having the stoichiometry Q_2MX_2 have been isolated with M = Hg,[20–22] Zn,[21] and Ni[22] and X = halide. Implied in this formulation is the $[MQ_2]^{2+}$ entity, the terminal oxidized member **8** of the electron-transfer series. We have carried out a thorough examination of the potential series **4–8** utilizing as ligands the deprotonated forms of pyrocatechol and tetrachloropyrocatechol with the principal aim of investigating the existence of each of the members of this electron-transfer series.

Experimental Section

Preparation of Compounds.—In the following reactions all operations leading to the formation of the complex and isolation of the final product were carried out using degassed solutions and solvents and under an atmosphere of nitrogen which had been rigorously freed of oxygen. Complexes derived from tetrachloropyrocatechol were purified without exclusion of oxygen while the complexes derived from pyrocatechol were purified and stored under an atmosphere of oxygen-free nitrogen. Reagent grade pyrocatechol was used without further purification. Tetrachloropyrocatechol was prepared according to the method of Jackson and MacLaurin.[23] Tetrachloro-*o*-benzoquinone was obtained from Aldrich Chemical Co. and recrystallized from ethyl ether before use. Phenanthrene-9,10-diol was prepared by the method of Schmidt and Lump.[24]

$[(n\text{-}C_3H_7)_4N]_2[Co(C_6Cl_4O_2)_2]$.—Tetrachloropyrocatechol (6.4 g, 26 mmoles) was dissolved in 120 ml (60 mmoles) of 10% aqueous tetra-*n*-propylammonium hydroxide solution. This solution was added to a stirred solution of 3.47 g (12.9 mmoles) of cobalt(II) nitrate hexahydrate in 50 ml of water. A violet-colored tar formed immediately. Dichloromethane (150 ml) was added and the solution stirred vigorously for 15 min. The dark red organic layer was separated and reduced at room temperature to a volume of ~15 ml, during which process reddish crystals formed. These were collected and recrystallized twice from dry dichloromethane. After drying at 56° (0.01 mm) for 24 hr, 7.6 g (69%) of brick-red crystals were obtained; mp 224° dec.

Anal. Calcd: C, 46.84; H, 6.11; N, 3.04. Found: C, 46.79; H, 5.95; N, 2.87.

$[(n\text{-}C_3H_7)_4N]_2[Ni(C_6Cl_4O_2)_2]$.—A solution of 8.05 g (32.5 mmoles) of tetrachloropyrocatechol in 150 ml (74 mmoles) of a 10% aqueous tetra-*n*-propylammonium hydroxide solution was added rapidly to 3.86 g (20.1 mmoles) of nickel acetate dissolved in 50 ml of water and 150 ml of ethanol. Under vigorous stirring for 2 hr a brown crystalline precipitate was formed. The crystals were collected on a frit, washed twice with 15-ml portions of water, and dried under pump vacuum. They were then recrystallized twice from dry dichloromethane and dried at 60° (10^{-3} mm) for 24 hr. A nearly quantitative yield of brown crystals was obtained; mp 219° dec.

Anal. Calcd: C, 46.84; H, 6.11; N, 3.04; Ni, 6.36. Found: C, 47.11; H, 6.29; N, 3.02; Ni, 6.28.

$[Ni(C_6Cl_4O_2)_2]$.—Tetrachloro-*o*-benzoquinone (3.0 g, 12.2 mmoles) was suspended in 50 ml of dry air-free *n*-hexane. After cooling to 0° 1.1 g (6.5 mmoles) of nickel carbonyl was added

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[9] Excluded from this statement are metal ions in pure oxide and mixed oxide crystals and in periodate and heteropoly salts in which higher formal oxidation states (*e.g.*, Ni(IV) and Cu(III)), are recognized; *cf.*, *e.g.*, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, Chapter 29.

[10] For a complete listing of references to simple and complex salts of pyrocatecholate dianion (prior to 1929) see "Beilstein's Handbuch der organischen Chemie," Band 6.

[11] R. Willstätter and F. Müller, *Ber.*, **41**, 2581 (1908).

[12] R. Weinland and A. Döttinger, *Z. Anorg. Allgem. Chem.*, **102**, 223 (1918).

[13] R. Weinland and A. Döttinger, *ibid.*, **111**, 167 (1920).

[14] H. Reihlen, *ibid.*, **123**, 173 (1922).

[15] E. Spacu and M. Kuras, *J. Prakt. Chem.*, **141**, 201 (1934).

[16] R. Weinland and E. Walter, *Z. Anorg. Allgem. Chem.*, **126**, 141 (1923); P. Pfeiffer, H. Simons, and E. Schmitz, *ibid.*, **256**, 318 (1948).

[17] E. Sellés, *Anales Soc. Españ. Fis. Quim.*, **37**, 114 (1941).

[18] J. D. Bu'Lock and J. Harley-Mason, *J. Chem. Soc.*, 2248 (1951).

[19] R. Criegee and K. Klonk, *Ann.*, **564**, 1 (1949).

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[22] P. J. Crowley and H. M. Haendler, *Inorg. Chem.*, **1**, 904 (1962).

[23] C. L. Jackson and R. D. MacLaurin, *Am. Chem. J.*, **37**, 11 (1907).

[24] J. Schmidt and H. Lump, *Ber.*, **43**, 790 (1910).

and the mixture stirred for 8 hr at 0°. Carbon monoxide was slowly evolved and a blue-green microcrystalline powder was formed. The product was collected by filtration and dried at 25° (10^{-3} mm) for 3 hr; 3.1 g (93%) of product was obtained. It could not be recrystallized due to its low solubility in those nonpolar solvents in which it is stable.

Anal. Calcd: C, 26.19; H, 0.00; Ni, 10.67. Found: C, 26.36; H, 0.44; Ni, 10.47.

$[(n\text{-}C_3H_7)_4N][Ni(C_6Cl_4O_2)_2]$.—$Ni(C_6Cl_4O_2)_2$ (0.7358 g, 1.357 mmoles) and 1.237 g (1.337 mmoles) of $[(n\text{-}C_3H_7)_4N]_2[Ni(C_6Cl_4O_2)_2]$ were mixed together in 30 ml of dry air-free dichloromethane. An intense brown solution developed immediately. The solution was stirred for 10 min, after which time there was no detectable solid in the reaction mixture. The solution was reduced to dryness by evaporation *in vacuo* at room temperature. The product (1.95 g, 99%) was obtained as a dark brown material. Its excessive solubility in weakly polar solvents prevented effective crystallization. The compound decomposes at ~150° without melting.

Anal. Calcd: C, 39.12; H, 3.83; N, 1.90; Ni, 7.97. Found: C, 38.52; H, 4.13; N, 1.91; Ni, 7.95.

$[(n\text{-}C_3H_7)_4N]_2[Cu(C_6Cl_4O_2)_2]$.—A solution of 7.4 g (30 mmoles) of tetrachloropyrocatechol dissolved in 125 ml (61 mmoles) of a 10% aqueous tetra-*n*-propylammonium hydroxide solution was added with stirring to a solution of 3.75 g (15 mmoles) of cupric sulfate pentahydrate in 70 ml of water. A light green precipitate was formed. This was collected and recrystallized from 300 ml of dichloromethane–ethanol (1:1 v/v). The crystallization was repeated using 200 ml of dry dichloromethane yielding olive-green needles (5.6 g, 40%) which were dried at 56° (0.01 mm) for 20 hr; dec pt 198°.

Anal. Calcd: C, 46.59; H, 6.08; N, 3.02. Found: C, 46.59; H, 6.02; N, 2.78.

$[(n\text{-}C_3H_7)_4N]_2[Zn(C_6Cl_4O_2)_2]$.—Zinc nitrate hexahydrate (4.45 g, 15 mmoles) was dissolved in 40 ml of water. To this solution a solution of 7.4 g (30 mmoles) of tetrachloropyrocatechol in 130 ml (64 mmoles) of 10% aqueous tetra-*n*-propylammonium hydroxide was added with stirring, yielding a white precipitate. Dichloromethane (200 ml) was added. After 5 min of stirring the organic layer was separated and filtered. The solvent was evaporated and the residue recrystallized twice from 20 ml of dichloromethane. The white crystals which were obtained were dried at 56° (0.01 mm) for 24 hr, yielding 5.3 g (38%); mp 222° dec.

Anal. Calcd: C, 46.50; H, 6.07; N, 3.01. Found: C, 46.57; H, 6.10; N, 2.71.

$[(n\text{-}C_3H_7)_4N]_2[Cd(C_6Cl_4O_2)_2]$.—A solution of 3.42 g (15 mmoles) of hydrated cadmium chloride in 150 ml of water was prepared. To it was added with stirring a solution of 7.4 g (30 mmoles) of tetrachloropyrocatechol in 130 ml (61 mmoles) of 10% aqueous tetra-*n*-propylammonium hydroxide. A voluminous white precipitate was formed which became progressively more crystalline as the reaction mixture was stirred for 2 days. At this point the precipitate was collected, washed with water, and dissolved in 25 ml of dichloromethane. This solution was added slowly to a mixture of 30 ml of benzene and 15 ml of dichloromethane. A crystalline product was obtained by refluxing the slurry produced for 30 min followed by slow cooling. The product was collected and further purified by Soxhlet extraction with a mixture of 10 ml of dichloromethane and 30 ml of benzene. The yellowish crystals obtained were dried at 80° (10^{-3} mm) for 10 hr to yield 7.9 g (56%) of light yellow product; mp 207° dec.

Anal. Calcd: C, 44.26; H, 5.78; N, 2.87. Found: C, 43.87; H, 5.76; N, 2.62.

$[(C_6H_5)_4As][B(C_6H_4O_2)_2]$.—The material formulated as $H[B(C_6H_4O_2)_2]$ was prepared according to Meulenhoff[25] and purified by sublimation at 130° (0.01 mm), which yielded white, air-stable crystals. This compound (3.0 g, 13 mmoles) was dissolved in 16 ml (18 mmoles) of 10% aqueous tetramethylammonium hydroxide solution. Tetraphenylarsonium chloride (5.87 g, 14 mmoles) in 30 ml of water was added, giving white crystals which were collected and washed with water. The product was dissolved in dichloromethane; the solution was concentrated by evaporation *in vacuo* and heated to boiling. Cooling yielded white crystals, which were collected, washed with benzene, and dried at 100° (0.001 mm) for 6 hr; 5.3 g (66%) of product was obtained; mp 195–197°.

Anal. Calcd: C, 70.84; H, 4.62; As, 12.27. Found: C, 71.37; H, 4.87; As, 11.82.

$[(C_6H_5)_4As]_3[Al(C_6H_4O_2)_3]$.—Aluminum chloride (0.8 g, 6 mmoles) was dissolved in 100 ml of water. To this solution was added 46 ml (50 mmoles) of a 10% aqueous solution of tetramethylammonium hydroxide followed by 2.2 g (20 mmoles) of pyrocatechol, giving a clear solution. Tetraphenylarsonium chloride (8.0 g, 19 mmoles) in 50 ml of water was added with stirring. Slightly yellow crystals separated immediately. These were collected, washed thoroughly with water, and dried at 40° (0.01 mm) for 6 hr to give a yellow powder. The product was purified by Soxhlet extraction with 25 ml of acetonitrile. The crystalline product was collected, washed with 10 ml of acetonitrile, and dried at 100° (10^{-3} mm) for 6 hr to yield 5.4 g (60%) of yellow crystals; mp 291–293°.

Anal. Calcd: C, 72.00; H, 4.83; As, 14.97. Found: C, 71.51; H, 5.06; As, 14.73.

$[(C_6H_5)_4As]_2[Mg(C_6H_4O_2)_2]$.—To a solution of 1.21 g (11 mmoles) of pyrocatechol in 30 ml (33 mmoles) of 10% aqueous tetramethylammonium hydroxide solution was added 0.6 g (5 mmoles) of magnesium sulfate in 10 ml of water. The colorless and nearly clear solution was filtered and 4.6 g (11 mmoles) of tetraphenylarsonium chloride in 50 ml of water was added to it to yield a flocculent precipitate. On standing overnight large light yellow crystals formed. The cloudy solution was decanted from the crystals which were then washed with three 5-ml portions of water and dried. The product was subjected to Soxhlet extraction with a mixture of 5 ml of benzene and 10 ml of dichloromethane. The extract was filtered, its volume reduced under diminished pressure to ~7 ml, and then heated to boiling. Slow cooling gave slightly yellow crystals which were dried at 100° (10^{-3} mm); 1.6 g (32%) of product was obtained; mp 201–204°.

Anal. Calcd: C, 71.56; H, 4.80; As, 14.88. Found: C, 70.79; H, 4.77; As, 14.73.

$[(n\text{-}C_3H_7)_4N]_2[Ni(C_6H_4O_2)_2]$.—Nickel acetate tetrahydrate (12.5 g, 50.3 mmoles) and 11.6 g (105 mmoles) of pyrocatechol were dissolved in 100 ml of water. To this solution was added with slow stirring 20 ml (300 mmoles) of 29% aqueous ammonia. After several minutes a green crystalline precipitate formed. This was collected and dissolved in 200 ml (100 mmoles) of a 10% aqueous tetra-*n*-propylammonium hydroxide solution. The water and ammonia were removed at room temperature under a pressure of 0.3 mm to a point at which ~20 ml of solution containing a brown microcrystalline material remained. The product was filtered off and dissolved in 70 ml of dichloromethane, the solution was filtered, and the volume was decreased to 10 ml by evaporation under reduced pressure. The brown crystals formed were collected, dried for 8 hr at 70° (0.01 mm), and recrystallized from dichloromethane to yield 9.9 g (30%); mp 188° dec.

Anal. Calcd: C, 66.77; H, 9.96; N, 4.33; Ni, 9.07. Found: C, 65.87; H, 9.71; N, 4.27; Ni, 8.84.

$[Ni(C_6H_4O_2)_2]$.—To a stirred solution of 2.2 g (20 mmoles) of pyrocatechol in 50 ml of water was added a solution of 20 g (80 mmoles) of nickel acetate tetrahydrate in 50 ml of water followed by a solution of 5.4 g (20 mmoles) of potassium persulfate in 100 ml of water. The reaction mixture became intensely green immediately. After 20 min it was filtered, the greenish black precipitate was washed with four 200-ml portions of water, and the product was dried at 56° (10^{-3} mm) for 6 hr. A nearly quantitative yield of black powder was obtained. The product was insoluble in all common solvents and could not be purified further.

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[25] J. Meulenhoff, *Rec. Trav. Chim.*, **44**, 150 (1925). For a discussion of the identity of the precursor of this compound, *cf.* H. Schäfer, *Z. Anorg. Allgem. Chem.*, **259**, 255 (1949).

Anal. Calcd: C, 52.43; H, 2.93. Found: C, 52.40; H, 3.42.

$[(n\text{-}C_3H_7)_4N]_2[Cu(C_6H_4O_2)_2]$.—Cupric chloride dihydrate (17 g, 100 mmoles) dissolved in 20 ml of water was added with slow stirring to a solution prepared from 33 g (300 mmoles) of pyrocatechol and 40 ml of 29% aqueous ammonia in 150 ml of water. The solution was cooled in the refrigerator overnight to yield green crystals which were collected, washed with two 3-ml portions of water, and dissolved in 240 ml (118 mmoles) of 10% aqueous tetra-*n*-propylammonium hydroxide solution. Water and ammonia were evaporated at room temperature under 0.1 mm, yielding olive-green crystals in ~30 ml of solution. The crystals were collected and washed with two 2-ml portions of water and with 5 ml of ether. The product was dried for 15 min at 10 mm and room temperature and then recrystallized from 25 ml of dry dichloromethane. The green crystals obtained were dried at 56° (0.01 mm) for 3 hr; 6.3 g (10%) of product was obtained; mp 191–192° dec.

Anal. Calcd: C, 66.27; H, 9.89; N, 4.29. Found: C, 65.48; H, 9.83; N, 4.51.

$[(C_6H_5)_4As]_2[Zn(C_6H_4O_2)_2]$.—To a solution of 2.82 g (9.5 mmoles) of zinc nitrate hexahydrate and 2.09 g (19 mmoles) of pyrocatechol in 150 ml of water was added a solution of 2.1 g (52 mmoles) of sodium hydroxide in 15 ml of water. The complex was precipitated from the colorless and completely clear solution by the addition with slow stirring of 9.5 g (23 mmoles) of tetraphenylarsonium chloride in 100 ml of water. The yellow crystals were collected, washed with four 100-ml portions of water, and dried at 50° (10^{-3} mm) for 9 hr and at 140° (10^{-3} mm) for 1 hr. A yellow-orange crystalline product (7.3 g, 76%) was obtained; mp 213–214° dec.

Anal. Calcd: C, 68.75; H, 4.62; As, 14.29. Found: C, 67.94; H, 4.78; As, 13.97.

$[Zn(C_6H_4O_2)_2]$.—The compound was prepared according to the directions of Bu'Lock and Harley-Mason[18] and was dried at 56° (0.005 mm) for 6 hr. A black powder resulted which was insoluble in all common solvents and could not be purified.

Anal. Calcd: C, 51.19; H, 2.86; Zn, 23.1. Found: C, 51.51; H, 2.31 (lit.[18] C, 52.2; H, 3.0; Zn, 23.7).

$[(n\text{-}C_3H_7)_4N]_2[Ni(C_{14}H_8O_2)_2]$.—Phenanthrene-9,10-diol (5 g, 24 mmoles) was dissolved in 200 ml of 95% ethanol, and to this solution was added 120 ml (60 mmoles) of 10% aqueous tetra-*n*-propylammonium hydroxide solution. A clear red solution resulted. Over 30 min 2.86 g of $NiCl_2 \cdot 6H_2O$ in 15 ml of water was added dropwise with stirring. The resulting dark brown solution and brown precipitate were stirred overnight, during which the color changed to a reddish brown. The volume was reduced by ~100 ml under vacuum at room temperature, and the resultant red-brown precipitate was collected, washed with water, and dried at 25° (0.01 mm). The crude product was boiled with 300 ml of dry dichloromethane and the hot solution filtered. Volume reduction to ~80 ml followed by cooling afforded the product as red crystals which were collected and washed with two 6-ml portions of dichloromethane. Soxhlet extraction with 25 ml of dichloromethane gave in good yield the final product as dark red sparkling crystals. Analysis indicated that the crystals contained $2CH_2Cl_2$/Ni.

Anal. Calcd: C, 63.73; H, 7.53; N, 2.75; Ni, 5.77. Found: C, 63.16; H, 7.60; N, 2.97; Ni, 5.72.

$Ni[3,5\text{-}(t\text{-}C_4H_9)_2C_6H_2O_2]_2$.—To a solution of 2.2 g (10 mmoles) of 3,5-di-*t*-butyl-*o*-benzoquinone[26] in 175 ml of *n*-pentane and 25 ml of benzene was added 0.8 ml (6 mmoles) of $Ni(CO)_4$ in 20 ml of benzene. The solution turned deep green as carbon monoxide was rapidly evolved. After 24-hr standing the solution was filtered and the solid collected was washed with *n*-heptane and acetone. It was then extracted twice into dichloromethane solution. The greenish brown product crystallized during the extraction; it was collected and dried *in vacuo*.

Anal. Calcd: C, 67.35; H, 8.07. Found: C, 67.17; H, 8.23.

$[(n\text{-}C_3H_7)_4N]_3[Fe(C_6Cl_4O_2)_3]$.—Ferrous sulfate heptahydrate (2.78 g, 10 mmoles) was dissolved in 70 ml of water. A solution of 7.4 g (30 mmoles) of tetrachloropyrocatechol in 125 ml (61 mmoles) of 10% aqueous tetra-*n*-propylammonium hydroxide was added with stirring. Dichloromethane (120 ml) was then added, giving a red layer which was separated and filtered, and the solvent was completely evaporated. The black-violet residue was dissolved in a mixture of 100 ml of dichloromethane and 75 ml of benzene; the solution was filtered, 300 ml of benzene was added, and the solution was refluxed for 15 min. Slow cooling afforded shiny violet crystals which were collected and redissolved in 50 ml of dichloromethane and 50 ml of benzene. This solution was filtered when hot. Benzene (125 ml) was added to the hot filtrate and the solution refluxed for 15 min. The violet crystalline product was obtained by filtration of the hot solution; the product was dried for 10 hr at 56° (10^{-3} mm); yield, 4.6 g (34%); mp 179–181°.

Anal. Calcd: C, 47.95; H, 6.26; N, 3.10. Found: C, 47.67; H, 6.16; N, 3.04.

Properties of Complexes. (a) **Solubility.**—The tetrapropylammonium salts of the pyrocatechol complexes are generally very soluble in water and dichloromethane. The corresponding tetrachloropyrocatechol complexes are insoluble in water but readily soluble in dichloromethane. Tetraphenylarsonium salts are insoluble in water but moderately soluble in dichloromethane except for the Ni and Al complexes, which are only slightly soluble, and the Zn complex, which is extremely soluble. Neutral pyrocatechol complexes are insoluble in all common solvents; $Ni(C_6Cl_4O_2)_2$ is slightly soluble in dichloromethane.

(b) **Oxidative Stability.**—Alkaline solutions of free pyrocatechol and tetrachloropyrocatechol are very air sensitive. The detection of *o*-benzosemiquinone and other oxidation products has been described.[27] All dinegative tetrachloropyrocatechol complexes are air stable as solids and in solution except for those of Co and Cd in dichloromethane. Pyrocatechol complexes of B, Mg, Al, and Zn are air stable as solids and in inert dry solvents. In solution they are oxidized in the presence of water producing a green color. Dinegative Cu and Ni pyrocatechol complexes are air sensitive in both the solid and solution phases.

(c) **Hygroscopicity.**—The pyrocatechol complexes, especially the Zn complex, are hygroscopic but can be handled in the air for very brief periods if not oxygen-sensitive.

Physical Measurements.—Magnetic measurements were performed by the Gouy method using an aqueous $NiCl_2$ solution as the calibrant. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Conductivities were measured in nitromethane using a Serfass conductivity bridge. A Varian Model V-4502 spectrometer was employed for the electron spin resonance measurements. Hyperfine splittings and *g* values were measured using a standard dual cavity arrangement with $[NiS_4C_4(CF_3)_4]^-$ and $[VS_6C_6(CF_3)_6]^-$, whose *g* values have been accurately measured previously in dichloromethane and acetonitrile,[4a,28] as the references.

Polarographic measurements in acetonitrile and DMSO were made using a rotating platinum electrode (rpe) as previously described[3a] with half-wave potentials recorded *vs.* a saturated calomel electrode. A glass-imbedded platinum wire, filed nearly flush with the glass shaft to which it is attached, served as the working electrode; it was rotated at 600 rpm. In these solvents most of the complexes studied revealed poorly defined oxidative or reductive waves whose shapes were frequently indicative of electrode coating; erratic diffusion currents were obtained which did not correspond to integral numbers of electrons involved in the electrode reactions. In an attempt to improve polarographic behavior, dichloromethane was employed as a solvent with the aims of retaining the integrity of the dissolved species and providing a medium in which the electrode reaction products would be more stable and soluble. Although these aims were not fulfilled for all systems studied, a general

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[26] K. Ley and E. Müller, *Ber.*, **89**, 1402 (1956).

[27] F. R. Hewgill, T. J. Stone, and W. A. Waters, *J. Chem. Soc.*, 408 (1964).

[28] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).

improvement in polarographic behavior was found. A practical method of polarographic measurements in dichloromethane has been developed which provides stable, reproducible diffusion currents and half-wave potentials reliable for internal comparison. The only previous polarographic work in this solvent is by Peover,[29a] who reduced quinones at a dropping mercury electrode, and Shriver and Posner,[29b] who studied several Fe(II) complexes at a platinum wire electrode.

Measurements in dichloromethane solution were made using an ORNL Model 1988 polarograph equipped with a three-electrode configuration and the same platinum working electrode. The polarographic cell is detailed in Figure 1. The compartments a and b are filled with the sample solution, which is $\sim 10^{-3}$–10^{-4} M in electroactive species and 0.10 M in $(n\text{-}C_4H_9)_4NPF_6$, the supporting electrolyte. The compartment b and the reference compartment c are connected *via* the salt bridge h composed of silica gel impregnated with a 0.42 M dichloromethane solution of the supporting electrolyte. This compound was prepared as follows. To a solution of 100 g of tetra-*n*-butylammonium bromide in 2 l. of water was added with stirring 51 g of NH_4PF_6 dissolved in 400 ml of water. The white precipitate was collected and washed with water until the filtrate was free of bromide. The product was dissolved in 400 ml of dichloromethane and this solution shaken with 500 ml of water. The organic phase was separated and its volume reduced to ~150 ml. Slow cooling to 0° afforded colorless crystals which were filtered off, washed with carbon tetrachloride, and dried over P_2O_5. A yield of 92 g (75%) was obtained; mp 247–248°. A further crop of satisfactory purity can be obtained by concentration of the filtrate.

The reference electrode system was prepared by shaking silver iodide with 10 ml of a dry dichloromethane solution 0.42 M in $(n\text{-}C_4H_9)_4NPF_6$ and 0.05 M in $(n\text{-}C_4H_9)_4NI$. Some of the silver iodide is observed to dissolve. This heterogeneous mixture is placed in the reference compartment c containing the silver electrode j. Compartments b and c are connected by insertion of the bridge h, and the pressure in each compartment is equalized by the stopcocks l, which are then closed. The sample compartment may then be purged or blanketed with dry nitrogen as desired. Measurements were made using a rotating platinum electrode inserted through d. In initial experiments the reference half-cell was allowed to equilibrate for 24 hr and its stability monitored thereafter by the potentials of the successive one-electron oxidations of $[CrS_6C_6(CN)_6]^{3-}$.[30] The following potentials were obtained for the two oxidative couples: 24 hr, +0.38, +0.92 v; 72 hr, +0.29, +0.83 v; after 72 hr, +0.29 ± 0.01, +0.83 ± 0.01 v, with this reproducibility maintained for at least 3 months. Reproducibility of the reference half-cell potential is accompanied by the formation of a crystalline white precipitate which is believed to be the soluble silver-containing species involved in the electrode reaction. This material was synthesized by refluxing an excess of AgI with 5.0 g of $(n\text{-}C_4H_9)_4NI$ in 100 ml of dichloromethane, filtering the hot solution, and cooling to 0°. Colorless crystals were isolated, mp 140–142°. Analysis indicated the approximate composition $(n\text{-}C_4H_9)_4NI \cdot 3AgI$. A reference half-cell prepared by saturating a 0.42 M $(n\text{-}C_4H_9)_4NPF_6$ dichloromethane solution with this material and silver iodide when used with the oxidative couples above yielded the quoted reproducible potential values within 72 hr. The only difference in the half-cells prepared by the two methods is the rate of attainment of equilibrium. The characteristics of the cell were checked by reducing a number of quinones studied by Peover.[29] Well-defined first-reduction waves were observed with diffusion currents consistent with one-electron processes. Increasing supporting electrolyte concentration to 0.5 M decreased the slopes of log $i(i_d - i)^{-1}$ *vs.* E plots somewhat and shifted $E_{1/2}$ values by $\sim\pm 50$ mv. The iR drop in the cell is not completely compensated by the three-electrode geometry. Because only internal comparisons of $E_{1/2}$ values were sought, these potentials were measured in 0.1 M solutions (greatly conserving supporting electrolyte). Quinone reduction potentials in dichloromethane and acetonitrile exhibited an excellent linear dependence described by $E_{1/2}(CH_2Cl_2) = E_{1/2}(CH_3CN) + 0.16$. The particular advantages of the experimental arrangement are its simplicity, convenience, and avoidance of contamination of either half-cell. Significantly, the reference half-cells are advantageous compared to that used by Peover[29a] inasmuch as the stability and reproducibility of their potentials are excellent and are unaffected by light and solvent evaporation. The useful potential range of dichloromethane is from −1.5 v to at least +3.0 v relative to the reference half-cell.

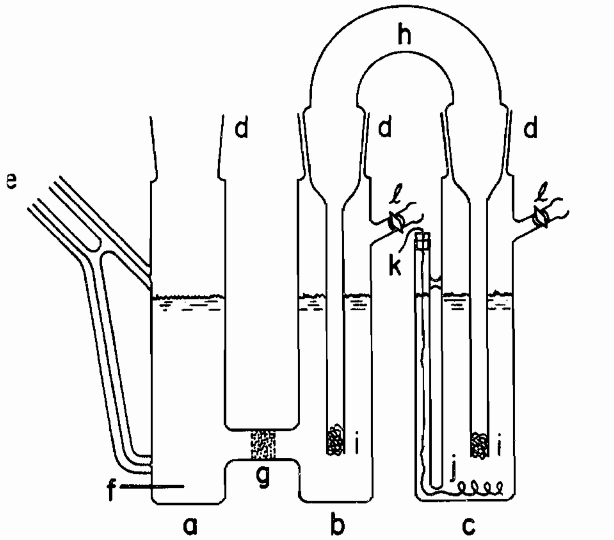

Figure 1.—Polarographic cell for measurements in dichloromethane solution: a, sample compartment (1.5 × 10 cm); b, junction compartment (containing sample solution); c, reference compartment; d, standard taper joints 14/20; e, capillary tubes for nitrogen purging and blanketing; f, platinum wire auxiliary electrode; g, medium porosity glass frit; h, solvent bridge; i, glass wool plugs; j, silver wire reference electrode; k, cork; l, pressure equilization stopcocks.

Results and Discussion

To support by analogy the appropriateness of our search for the members **4**–**8**, we point out very briefly some representative findings in other series of the same type. In the $[M\text{–}S_4]^z$ series the nickel complexes $Ni(tdt)_2$ (**2**) with $z = -2, -1$,[7] and 0[31] are known. The $z = -2, -1, 0, +1$ species of $[NiS_4C_4(C_6H_5)_4]$ have been isolated or detected polarographically in dichloromethane.[32] For $[MS_4C_4(CN)_4]$ the $z = -2, -1, 0$ members have been established for M = Ni.[3a,b,c,32] Evidence from polarography or direct preparation has demonstrated in the $[M\text{–}N_4]^z$ series the existence of the $z = -2, -1, 0, +1, +2$ members with M = Ni, Pd, and Pt, all three metals being coordinated to the *o*-$C_6H_4(NH)_2$ ligand system. Our results bearing on the scope of the electron-transfer series of the $[M\text{–}S_4]^z$, $[M\text{–}N_4]^z$, and $[M\text{–}S_2O_2]^z$ types will be presented shortly.[32] Suffice it to say that there is ample foundation by analogy for the existence of

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[29] (a) M. E. Peover, *Proc. Chem. Soc.*, 167 (1963); *Trans. Faraday Soc.*, **60**, 417 (1964); (b) D. F. Shriver and J. Posner, *J. Am. Chem. Soc.*, **88**, 1672 (1966).

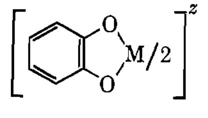
[30] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **86**, 2799 (1964).

[31] E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965).

[32] A. L. Balch and R. H. Holm, to be published.

an $[M–O_4]^z$ series. The results which follow show, however, that the well-defined electron-transfer properties of other series, notably $[M–S_4]^z$ and $[M–N_4]^z$, do not obtain here.

Our investigations have involved the bis(pyrocatecholato) ($M(cat)_2{}^z$), bis(tetrachloropyrocatecholato) ($M(Clcat)_2{}^z$), and bis(phenanthrene-9,10-diolato)-($Ni(phenan)_2{}^z$) complexes **9**, **10**, and **11**, respectively. The existence and properties of each group of complexes defined by its charge z are considered in turn.



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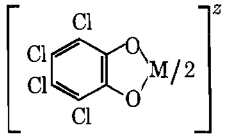

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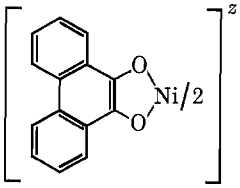

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$[M–O_4]^{2-}$ Complexes.—As already mentioned a large number of salts apparently containing $M(cat)_2{}^{2-}$ have been isolated.[12–17] The published procedures reveal no uniform synthetic approach, no consistent effort to exclude air from the oxidatively unstable products, and the formulation of products in terms of sufficient additional components (water, excess catechol, alkali hydroxide) to fit analytical results. Accordingly, we set forth in detail in the Experimental Section a consistent synthetic approach, carried out under anaerobic conditions, which leads to the isolation of crystalline tetrapropylammonium or tetraphenylarsonium salts free of excess components. The $M(cat)_2{}^{2-}$ salts, M = Mg, Ni, Cu, Zn, were prepared. Because of their much greater oxidative stability, notably in solution, $M(Clcat)_2{}^{2-}$ complexes (M = Co, Ni, Cu, Zn, Cd) were also prepared.

TABLE I

CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITY DATA

Complex	Λ^a	μ_{eff}, BM^b
$[(n\text{-}C_3H_7)_4N]_3Fe(Clcat)_3$	196	5.93
$\{[(n\text{-}C_3H_7)_4N]_2Co(Clcat)_2\}_n$	*c*	4.96
		4.94 (CH_2Cl_2 soln, 25°)
$[(n\text{-}C_3H_7)_4N]_2Ni(Clcat)_2$	136	Diamagnetic
$[(n\text{-}C_3H_7)_4N]Ni(Clcat)_2$	*c*	3.80
		3.88 (CH_2Cl_2 soln, 25°)
$Ni(Clcat)_2$	...	3.49
$Ni(cat)_2$	...	2.70
$Ni[3,5\text{-}(t\text{-}C_4H_9)_2(C_6H_2O_2)]_2$	...	3.92
$[(n\text{-}C_3H_7)_4N]_2Cu(Clcat)_2$	140	1.87
$[(n\text{-}C_3H_7)_4N]_2Cu(cat)_2$	*c*	1.87
$[(n\text{-}C_3H_7)_4N]_2Zn(Clcat)_2$	139	Diamagnetic
$[(n\text{-}C_3H_7)_4N]_2Cd(Clcat)_2$	126	Diamagnetic

[a] Cm^2 mole^{-1} ohm^{-1} in ~10^{-3} *M* CH_3NO_2 solution. [b] Data refer to solids at ~25° unless otherwise stated; diamagnetic susceptibilities not accurately determined. [c] Not stable in CH_3NO_2.

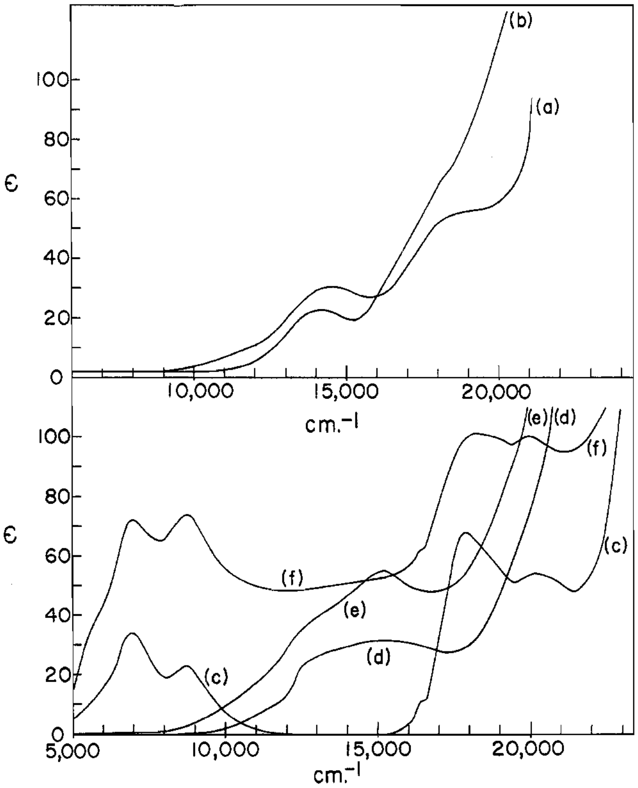

Figure 2.—Electronic spectra of $M(cat)_2{}^{2-}$ and $M(Clcat)_2{}^{2-}$ complexes. Spectra in dichloromethane solution: (a) $Ni(cat)_2{}^{2-}$, (b) $Ni(Clcat)_2{}^{2-}$, (c) $Co(Clcat)_2{}^{2-}$ (0.010 *M*), (d) $Cu(Clcat)_2{}^{2-}$, (e) $Cu(cat)_2{}^{2-}$; (f) Nujol mull of $[(n\text{-}C_3H_7)_4N]_2[Co(Clcat)_2]$ (absorbance scale arbitrary).

Some physical properties of these complexes are set out in Table I. Comparison with previous conductance data[3a,4a] indicates that the complexes behave as typical 2:1 electrolytes in nitromethane. The Zn and Cd species are conventional diamagnetic d^{10} complexes. $Co(Clcat)_2{}^{2-}$ was isolated as a reddish crystalline material and appears to have the same essential structure in the crystalline and solution phases, judging from the near constancy of the magnetic moments and spectra (*cf.* Figure 2) in the two phases. Approximate octahedral coordination of Co(II) is indicated by the magnetic moment, which is in the same range (4.9–5.0 BM) as those of bis(acetylacetonato)cobalt(II), $Co(acac)_2$, and its dihydrate,[33] both of which are known to contain octahedrally-coordinated Co(II).[34] The moment of the only known tetrahedral $Co–O_4$ complex, bis(dipivaloylmethanato)cobalt(II), $Co(DPM)_2$, is 4.34 BM.[35] The spectral appearance in the 15,000–23,000 cm^{-1} region strongly resembles that of $Co(acac)_2$ and $Co(acac)_2 \cdot 2H_2O$, whereas $Co(DPM)_2$ exhibits a structureless absorption feature at 18,000 cm^{-1}.[35] In the 5000–10,000 cm^{-1} region the two well-defined bands at 7000 and 8700 cm^{-1} are not found in the spectra of $Co(acac)_2$ and $Co(acac)_2 \cdot 2H_2O$, which show a broad absorption centered at ~8500 cm^{-1}.[35] The 7000 and 10,000 cm^{-1} absorption features in the $Co(DPM)_2$

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(33) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(34) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965); G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

(35) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).

spectrum are believed not related to the two near-infrared bands of $Co(Clcat)_2^{2-}$ because the high moment of the latter in solution precludes a significant concentration of tetrahedral species. It is concluded that $Co(Clcat)_2^{2-}$ exists as a polymerized species whose oligomer(s) contain roughly octahedral Co(II) and thus may be structurally similar to $Co(acac)_2$. We have been unable to purify salts of $Co(cat)_2^{2-}$, because of their extreme solubility.

The Ni(II) complexes $Ni(cat)_2^{2-}$, $Ni(Clcat)_2^{2-}$, and $Ni(phenan)_2^{2-}$ are of particular interest because they are among the very few $Ni–O_4$ species known which are monomeric and thus diamagnetic. The only other characterized complexes of this sort are certain bis(β-diketone) complexes which are significantly constrained from molecular association[36] or exist in both associated and monomeric forms.[37] The spectra of $Ni(cat)_2^{2-}$ and $Ni(Clcat)_2^{2-}$ shown in Figure 2 reveal the two lowest-energy spin-allowed ligand field absorptions at 14,500 and 19,000 and 14,150 and 18,200 cm^{-1}, respectively. These ligands lie more toward the weak field end of the spectrochemical series than do β-diketonates, whose complexes exhibit their lowest energy transition at 17,300–18,900 cm^{-1}.[36,37] Inasmuch as the first spin-allowed ligand field transition in planar $Ni–O_2N_2$ complexes is probably $\pi^* (x^2 - y^2) \rightarrow \sigma^* (xy)$,[38] it is likely that the lowest energy bands in $Ni(cat)_2^{2-}$, $Ni(Clcat)_2^{2-}$, and the β-diketone complexes should be assigned similarly.[39]

The Cu(II) complexes $Cu(cat)_2^{2-}$ and $Cu(Clcat)_2^{2-}$ are similar in electronic structure to bis(β-diketone) and bis(β-ketoester) Cu(II) complexes, which constitute the only other examples of monomeric $Cu–O_4$ species. The epr parameters, determined by measurements on glasses and fluid solutions,[40] are set out in Table II and emphasize this similarity, although the degree of σ covalency (*vide infra*) appears to be larger for $Cu(acac)_2$. Maxima in the ligand field spectra are located in the 12,500–15,200 cm^{-1} range (*cf.* Figure 2), again indicating that cat^{2-} and $Clcat^{2-}$ induce somewhat weaker ligand fields than do simple β-diketones, whose Cu(II) complexes exhibit maxima in the 14,000–18,000 cm^{-1} region.[41]

TABLE II

EPR DATA FOR $[Cu–O_4]$ COMPLEXES

	$[(n\text{-}C_3H_7)_4N]_2$-$Cu(cat)_2$[a]	$[(n\text{-}C_3H_7)_4]_2$-$Cu(Clcat)_2$[a]	$Cu(acac)_2$ Glass[b]	$Cu(acac)_2$ Single crystal[d]
$g_\parallel$	2.233	2.254	2.264	2.266
$g_\perp$	2.058	2.056	2.036	2.053
$\langle g \rangle$	2.118	2.124	2.112[c]	2.124[c]
$10^4 A_\parallel$, cm^{-1}	−205	−200	−145.5	−160
$10^4 A_\perp$, cm^{-1}	*e*	*e*	29	−19.5
$10^4\langle A \rangle$, cm^{-1}	82	79	68	66
α_2	0.86	0.87	0.72	

[a] All data obtained in 1:1 v/v $CHCl_3$–DMF; glass measurements at ~100°K. [b] Data from ref 40. [c] Calculated from anisotropic values. [d] Data from A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29,** 31 (1958). [e] Not directly measured.

$[M–O_4]^-$ Complexes.—The tendency of the $z = -2$ complexes to be oxidized to the $z = -1$ members, or to more highly oxidized species, has been assessed from their polarographic half-wave potentials, which are given in Tables III and IV. Our previous[3a,4a] and continuing[32] work in the $[M–S_4]^z$ series, as well as that by others,[7b] has shown that one-electron oxidation–reduction steps are readily detected polarographically and that the oxidation–reduction products can be chemically prepared provided that the half-wave potentials fall within a certain range.

TABLE III

POLAROGRAPHIC DATA FOR $[M(cat)_2]^z$ AND $[M(Clcat)_2]^z$ COMPLEXES IN DICHLOROMETHANE[a]

Complex	n(apparent)[b]	$E_{1/2}$, v	i_d/c, μa/mmole
$B(cat)_2^-$	1[i]	1.10	19
$Mg(cat)_2^{2-}$	2(?)	1.27	47[d]
$Al(cat)_3^{3-}$	?	0.38	32[d]
$Fe(Clcat)_3^{3-}$ [c]	1	0.37	16
	1	0.76	20
	1	1.10	16
$Cu(Clcat)_2^{2-}$	1	0.60	20
$Cu(cat)_2^{2-}$	1	0.07	21[d]
$Zn(Clcat)_2^{2-}$		*e, f*	
$Zn(cat)_2^{2-}$		*e, g*	
$Cd(Clcat)_2^{2-}$		*e, h*	

[a] Data refer to oxidation of ions in first column at rpe. [b] Apparent number of electrons involved in electrode process as inferred from diffusion currents. [c] Reduction to $z = -4$ species observed at −1.66 v in acetonitrile. [d] Drawn-out wave indicating irreversibility with $|E_{3/4} - E_{1/4}| > 100$ mv. [e–h] Poorly defined wave with no plateau beginning at 0.5 v (*f*), 0.1 v (*g*), 0.3 (*h*); wave shape indicates filming of electrode. [i] No radical could be detected from controlled potential electrolysis in an esr spectrometer.

Polarographic oxidation waves of $[M–O_4]^{2-}$ species in acetonitrile are generally poorly defined and are indicative of highly irreversible processes. On the assumption that the electrode reaction products might be unstable in acetonitrile, polarographic measurements were also performed in dichloromethane. A general improvement in wave shape was observed but somewhat drawn-out waves persisted. The number of electrons involved in the oxidative reactions has been inferred from a comparison of diffusion currents

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(36) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).

(37) L. Wolf and E. Butter, *Z. Anorg. Allgem. Chem.*, **339**, 191 (1965).

(38) J. Ferguson, *J. Chem. Phys.*, **34**, 611 (1961).

(39) This assignment has been made for the lowest energy ligand field band in a variety of planar Ni(II) complexes (*cf.* H. B. Gray and C. J. Ballhausen *J. Am. Chem. Soc.*, **85**, 260 (1963); B. G. Werden, E. Billig, and H. B. Gray, *Inorg. Chem.*, **5**, 78 (1966), and references cited therein), including $Ni(tdt)_2^{2-}$. *If* this assignment is correct for $Ni(cat)_2^{2-}$ *and* $Ni(tdt)_2^{2-}$, these complexes offer one of the rare cases in which to compare the relative positions of S and O in the spectrochemical series using ligands which are structurally identical except for the donor atoms. The one-electron orbital separation parameter, Δ_1, for $Ni(cat)_2^{2-}$ is readily calculated to be 17,300 cm^{-1}, the same value as for $Ni(tdt)_2^{2-}$ (using $F_2 = 10F_4 = 800$ cm^{-1}). Thus cat^{2-} and tdt^{2-} may occupy nearly the same spectrochemical position with respect to planar Ni(II), a result of some interest inasmuch as sulfur shows the greatest spread in spectrochemical position of any ligand (*cf.* C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962)). The only other equally close comparison involves $Cr(C_2O_4)_3^{3-}$ and $Cr(C_2O_2S_2)_3^{3-}$, whose *Dq* values differ by only ~3% but which show a substantial nephelauxetic difference (R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964)). While we feel that it is useful to make this spectral comparison in the event these assignments are verified, it is pointed out that at present there is no truly *direct* evidence for their correctness.

(40) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(41) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **2**, 102 (1963).

TABLE IV

POLAROGRAPHIC DATA FOR NICKEL COMPLEXES AND QUINONES IN ACETONITRILE AND DICHLOROMETHANE[a]

Species	n (apparent)[b]	CH_3CN $E_{1/2}$, v	CH_3CN i_d/c[c]	CH_2Cl_2 $E_{1/2}$, v	CH_2Cl_2 i_d/c[c]
$Ni(phenan)_2^{2-}$	2	-0.65	45		
	1			-0.38	19
$Ni(cat)_2^{2-}$	1	-0.38	24	-0.06	20
$Ni(Clcat)_2^{2-}$	2	0.15	41		
	1			0.48	26
9,10-Phenanthroquinone[d]	1	-0.65	*e*	-0.51	33
	1	-1.21	*e*	~ -1.3	*g*
1,2-Benzoquinone[d]	1	-0.31[f]	*e*	(-0.15)[h]	
	1	-0.90[f]	*e*	(-0.74)[h]	
Tetrachloro-1,2-benzoquinone[d]	1	0.14	*e*	0.30	25
	1	-0.61	*e*	~ -0.7	*g*
$Ni(tdt)_2^{2-}$	1	-0.58	34	-0.40	24
	1	*i*		0.52	22
$[NiS_4C_4(CN)_4]^{2-}$	1	0.23	27	0.30	21
	1	*i*		1.38	24

[a] Data refer to stepwise oxidation of anions, stepwise reduction of quinones. [b] Apparent number of electrons involved in electrode process as inferred from diffusion currents. [c] μa/mmole. [d] Reduction in acetonitrile at dme, in dichloromethane at rpe. [e] One-electron process, *cf.* M. E. Peover, *J. Chem. Soc.*, 4540 (1962). [f] Data from ref *e*. [g] Highly irreversible wave. [h] Not measured, calculated from acetonitrile potentials (see Experimental Section). [i] No well-defined wave corresponding to $-1 \rightarrow 0$ oxidation.

with those obtained for the established one-electron oxidations of $Ni(tdt)_2^{2-}$ and $[NiS_4C_4(CN)_4]^{2-}$ in acetonitrile and dichloromethane. The results shown in Tables III and IV reveal that, of the transition metal dianions, $Cu(cat)_2^{2-}$, $Cu(Clcat)_2^{2-}$, $Ni(phenan)_2^{2-}$, $Ni(cat)_2^{2-}$, and $Ni(Clcat)_2^{2-}$ undergo (probable) one-electron oxidations in dichloromethane. For purposes of direct comparison with nickel complexes of other series we attempted isolation of $Ni(Clcat)_2^-$ by chemical oxidation of the relatively stable $Ni(Clcat)_2^{2-}$ in dichloromethane.

Reaction of $[(n\text{-}C_3H_7)_4N]_2Ni(Clcat)_2$ and $Ni(Clcat)_2^0$ (*vide infra*) in dichloromethane afforded in quantitative yield a dark brown solid which analyzes satisfactorily as $[(n\text{-}C_3H_7)_4N]Ni(Clcat)_2$.[42] That this product is not a mixture of unreacted starting materials is evidenced by its extremely high solubility in dichloromethane ($Ni(Clcat)_2^0$ is very slightly soluble in this solvent), its absorption spectrum, which shows no evidence of either original complex, and its magnetic moment, which is practically the same in the solid and solution and considerably larger than that of $Ni(Clcat)_2^0$ itself. The product shows no polarographic oxidative or reductive behavior in dichloromethane. We infer from this last observation that the material does not contain a conventionally bonded monoanion (*viz.*, **10**, $z = -1$) which bears the same relationship to $Ni(Clcat)_2^{2-}$ as do $[Ni\text{-}S_4]^-$ species to $[Ni\text{-}S_4]^{2-,0}$ in a given $[Ni\text{-}S_4]^z$ series. However, that the above reaction proceeds at all seems indicative of some type of electron-transfer reaction. We suggest that, in the absence of other information, a reasonable formulation of the product may be a charge-transfer complex in which $Ni(Clcat)_2^{2-}$ acts as the donor and $Ni(Clcat)_2^0$ as the acceptor. A number of 1:1 complexes between conventional bis-chelate metal(II) complexes and organic π acceptors have been characterized[43] and their structures determined,[44] including that between bis-(8-hydroxyquinolinato)palladium(II) and *p*-chloranil.[44a] The reasonableness of observed magnetic moment in connection with a charge-transfer structure cannot presently be assessed.

Controlled potential electrolysis of the Ni dianions in dichloromethane at potentials appropriate for generation of the apparent monoanions failed to yield a detectable esr signal. The $Ni(Clcat)_2^0\text{-}Ni(Clcat)_2^{2-}$ reaction product in dichloromethane also produced no signal. $[Ni\text{-}S_4]^-$ complexes without exception give strong esr signals characteristic of their doublet ground states.[2-6] It is possible that any $[Ni\text{-}O_4]^-$ species produced may have triplet ground states and sufficiently short spin-lattice relaxation times that their spectra are not detectable at room temperature.

In our search for $[M\text{-}O_4]^-$ species containing metals other than nickel we have taken cognizance of the important results of Eaton,[45] who has shown that aerial oxidation of catechol solutions containing metal ions such as Zn^{2+}, Cd^{2+}, and Mg^{2+} produces a species of formulation $[M(cat)(H_2O)_n]^+$ in which the semiquinone is coordinated to the metal ion. Although the polarographic results for $M(cat)_2^{2-}$ and/or $M(Clcat)_2^{2-}$ complexes of these metals do not indicate any well-defined one-electron oxidations (*cf.* Table III), attempts were made to effect chemical generation of $[M\text{-}O_4]^-$ species by treatment of the dianions with 1 equiv of a one-electron oxidizing agent. Reaction of the complexes in dichloromethane with *o*-chloranil, TCNE, or $NiS_4C_4(CF_3)_4$ produced color changes, and signals due to the monoanion of the oxidant were usually evident. A second much weaker signal of width ~15 gauss at or near $g = 2.002$ was also observed, but the oxidation products of the catechol complexes exhibited no proton hyperfine splitting similar to that observed by Eaton.[45] The reaction of $Cd(Clcat)_2^{2-}$ and $NiS_4C_4(CF_3)_4$ yielded a radical with $\langle g \rangle = 2.002$ and apparent $^{111,113}Cd$ (25.2% abundance, $I = {}^1/_2$) satellite splitting of 7.6 gauss. Whether this radical is $Cd(Clcat)_2^-$ is not known. Finally, aerial oxidation of solutions of these complexes (and of $Al(cat)_3^{3-}$) gave a deep green color and an esr signal, the intensity of both of which was increased by very small amounts of water. The radicals were identified from their characteristic esr spectra to be *o*-benzosemiquinone and its further oxidation product.[27]

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(42) Note that this reaction is strictly analogous to that between $[NiS_4C_4(CF_3)_4]^{-2}$ and $[NiS_4C_4(CF_3)_4]^0$ in dichloromethane which gives a very high yield of $[NiS_4C_4(CF_3)_4]^-$. The product obtained from this reaction is identical with that from the iodine oxidation of the dianion or the acetone reduction[3a] of the neutral complex.

(43) (a) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962); (b) A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc.*, 2579 (1965).

(44) (a) B. Kamenar, C. K. Prout, and J. D. Wright, *ibid.*, 4851 (1965); (b) A. S. Bailey and C. K. Prout, *ibid.*, 4867 (1965); (c) C. K. Prout and H. M. Powell, *ibid.*, 4882 (1965).

(45) D. R. Eaton, *Inorg. Chem.*, **3**, 1268 (1964).

$[M–O_4]^0$ Complexes.—The reaction $Ni(CO)_4 + 2(CF_3)_2C_2S_2 \rightarrow NiS_4C_4(CF_3)_4$ proceeds rapidly and in high yield, suggesting that an analogous reaction with *o*-quinones might yield the intermediate members $[Ni–O_4]^0$ of the electron-transfer series. Reactions carried out using *o*-chloranil and 3,5-di-*t*-butyl-*o*-quinone afforded dark greenish products of composition Ni(quinone)$_2$. Also, persulfate oxidation of pyrocatechol in Zn^{2+} [18] and Ni^{2+} aqueous solutions produced dark-colored products of composition $M(cat)_2^0$. Except for the complex derived from the di-*t*-butylquinone, which is sparingly soluble in dichloromethane, these species are practically insoluble in all common organic solvents and for this reason cannot be satisfactorily purified. Polarographic experiments were possible only with $Ni(3,5\text{-}(t\text{-}C_4H_9)_2C_6H_2O_2)_2$ in dichloromethane. Unlike neutral complexes in the $[Ni–S_4]^z$, $[Ni–N_2S_2]^z$, and $[Ni–N_4]^z$ series, which are without known exception polarographically reducible to mono- and dianions and sometimes oxidizable to cationic species,[8,32] this complex shows no well-defined oxidation–reduction behavior in the range +2 to −1.6 v. An additional difference is the paramagnetism of the $[Ni–O_4]^0$ species and the diamagnetism of the neutral nickel complexes of the aforementioned three series. All of these results point toward a decided lack of similarity in both structure and oxidation–reduction propensity of the $[Ni–O_4]^0$ species when compared to the neutral nickel complexes of other series. The paramagnetism and extremely low solubility of these species strongly suggest a polymeric structure possibly involving six-coordinate Ni(II).[46]

$[M–O_4]^+$ Complexes.—The only information relating to the existence of such species has come from the polarographic oxidation of $Ni(Clcat)_2^{2-}$ in DMSO solution. Waves are observed at 0.17 and 0.78 v and correspond to apparent two- and one-electron reactions, respectively. This second wave is not observed in either acetonitrile or dichloromethane, nor is a corresponding wave observed for the other nickel complexes. The oxidized species effecting this wave must be considered unidentified, although the formation of $Ni(Clcat)_2^+$ in DMSO cannot be discounted. The potential of the wave is too positive to permit chemical preparation of the oxidation product. In comparison, electrochemical formation of a number of $[Ni–N_4]^+$ and several $[Ni–S_4]^+$ species and chemical isolation of iodide salts of the former species have been possible.[8,32]

$[M–O_4]^{2+}$ Complexes.—The principal evidence for the existence of this complex entity rests on the isolation of the complexes $NiBr_2 \cdot 2$phenan and $NiBr_2 \cdot 2$-chrysenequinone.[22] Also prepared was $ZnBr_2 \cdot$phenan, which was reformulated as $[Zn(phenan)_2][ZnBr_4]$.[22] Actual coordination of the quinone is indicated by definite decreases in the carbonyl stretching frequencies. The phenan complex of nickel bromide has a moment of 3.22–3.26 BM in the solid, thereby discounting any structure involving the nearly tetrahedral $NiBr_4^{2-}$ (3.80 BM[49]) and a normally paramagnetic cation (~3.3 BM). A reasonable formulation is evidently $[Ni(phenan)_2Br_2]$. It is noteworthy that the complexes are stable only as solids; dissolution in nonpolar solvents occurs only as a result of decomposition.[22] Our attempts to prepare $Ni(Clcat)_2^{2+}$ species using a published method[22] were not successful.

Influence of Ligand Structure on Half-Wave Potentials.—One of the most striking features of the behavior of $[MS_4C_4R_4]^z$ complexes belonging to the general $[M–S_4]^z$ electron-transfer series is the pronounced dependence of half-wave potentials on the nature of R. This situation is clearly shown by the potentials of the $-2 \rightarrow -1$ and $-1 \rightarrow 0$ couples for nickel complexes in dichloromethane, whose respective values vary from 0.30 and 1.38 v (R = CN) to −0.72 and 0.28 v (R = H). According to the arguments of Vlček,[50] the potentials of the oxidation–reduction couples of complexes behave with respect to substitution on the parent ligand system as would those of the free ligand couples. In the $[M–S_4]^z$ series it has not been possible to investigate the substituent dependence of the free ligand potentials due to the inability to observe the processes $R_2C_2S_2^{2-} \rightarrow R_2C_2S_2^-$ and $R_2C_2S_2^- \rightarrow R_2C_2S_2^0$. In the $[M–O_4]^z$ series the analogous ligand potentials (*e.g.*, $C_6Cl_4O_2^{2-} \rightarrow C_6Cl_4O_2^-$, $C_6Cl_4O_2^- \rightarrow C_6Cl_4O_2^0$) can be measured and thus are available for comparison with related processes in the $[M–O_4]^z$ series.

Considered are the potentials of the apparent one-electron oxidations of Cu and Ni complexes and free ligands in dichloromethane. The species are arranged below in order of increasing ease of oxidation and the potentials shown are differences between those for one-electron oxidations of the indicated species.

$$\overbrace{Cu(cat)_2^{2-} > Cu(Clcat)_2^{2-}}^{-0.53\text{ v}}$$

$$\overbrace{Ni(phenan)_2^{2-} > Ni(cat)_2^{2-}}^{-0.32\text{ v}} \quad \overbrace{ Ni(cat)_2^{2-} > Ni(Clcat)_2^{2-}}^{-0.54\text{ v}}$$

$$\overbrace{phenan^{2-} > cat^{2-}}^{-0.6\text{ v}} \quad \overbrace{cat^{2-} > Clcat^{2-}}^{-1.4\text{ v}}$$

$$\overbrace{phenan^- > cat^-}^{-0.36\text{ v}} \quad \overbrace{cat^- > Clcat^-}^{-0.45\text{ v}}$$

The most appropriate comparisons are between potentials for the ligand and complex dianions, from which it is seen that the order of oxidative stability of the complexes and ligands is the same and that the po-

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(46) Reactions of $Ni(CO)_4$ with some *p*-quinones in the presence and absence of chelating diolefins have been reported.[47] Reactions with duroquinone afforded Ni(duroquinone)$_2$[47a] (I) and (diolefin)Ni(duroquinone).[47b,c,d] It was noted that some *p*-quinones of higher electron affinity effected oxidation to Ni(II) salts[47a,c] and that *o*-quinones did not give products structurally similar to I.[47b] Because *o*-quinones are in general stronger oxidizing agents than their *para* counterparts (*e.g.*, compare potentials in Table IV and ref 48) the present findings appear consistent with these earlier results.

(47) (a) G. N. Schrauzer and H. Thyret, *J. Am. Chem. Soc.*, **82**, 6420 (1960); (b) G. N. Schrauzer and H. Thyret, *Z. Naturforsch.*, **16b**, 352 (1961); *ibid.*, **17b**, 72 (1962); (c) G. N. Schrauzer and H. Thyret, *Ber.*, **96**, 1755 (1963); (d) G. N. Schrauzer and H. Thyret, *Angew. Chem.*, **74**, 488 (1962).

(48) M. E. Peover, *J. Chem. Soc.*, 4540 (1962).

(49) L. Sacconi, M. Ciampolini, and F. Maggio, *Inorg. Chem.*, **4**, 407 (1965).

(50) A. A. Vlček, *Z. Anorg. Allgem. Chem.*, **304**, 109 (1960); *Progr. Inorg. Chem.*, **5**, 211 (1963).

tential difference between the ligands is attenuated by complexation. Both of these results agree with Vlček's conclusions.[30]

An interesting result of possibly general significance in the interpretation of half-wave potentials of electron-transfer complexes emerges from a consideration of the oxidation potentials of $Cu(cat)_2^{2-}$ and $Cu(Clcat)_2^{2-}$, which differ by a substantial amount. Cyclic voltammetry studies have demonstrated that the oxidations of these complexes are reversible or, at worst, quasi-reversible at a platinum electrode in dichloromethane.[51] Epr results have shown that these species are classical Cu(II) complexes with a $^2B_{1g}$ ground state. The covalency parameter α^2 relating to the MO of the odd electron in D_{2h} symmetry, $\psi(\sigma^*, b_{1g}) = \alpha d_{xy} - \alpha'\sigma_L(b_{1g})$, has been estimated for the two complexes from $A_{\|}$ data using the relationship[40,52]

$$\alpha^2 = -(A_{\|}/P) + (g_{\|} - 2.0023) + (3/7)(g_{\perp} - 2.0023) + 0.04$$

The results obtained using $P = 0.036\ cm^{-1}$ are shown in Table II and are the same within the uncertainty of the method. If it is accepted that the σ^* electron is the most loosely bound electron in the complexes and is removed in the electrochemical oxidation, it follows that substituent changes alone (*i.e.*, not necessarily accompanied by measurably different degrees of delocalization) can produce significantly different potentials. The finite amount of delocalization of the σ^* electron in the Cu(II) complexes results in different energies of $\psi(b_{1g})$ in the two cases, thereby leading to different potentials. The situation might be likened to the half-wave potentials of the oxidation of aromatic hydrocarbons, which vary linearly with the energy of the highest filled MO.[53] A similar situation could exist in the $[M-S_4]^z$ series, in which the dependence of $E_{1/2}$ on R (M constant) need not necessarily be intercepted as arising from significantly different degrees of delocalization of the electron to be removed in oxidation or added in reduction.

Existence of $[M-O_6]^z$ Series.—The existence of the general $[M-S_6]^z$ electron-transfer series is now well established and is composed of the groups $[MS_6C_6R_6]^z$,[28,30,54a,b] and $[M(tdt)_3]^z$.[54c] Examples include M = Cr, Mo, W, R = CF_3, C_6H_5, $z = -2, -1, 0$;[30,54a] M = V, R = CN, $z = -3, -2, -1$;[28] and $[ReS_6C_6(C_6H_5)_6]^z$, $z = -3, -2, -1, 0, +1$,[54c] presently the most extensive series of this general type. An attempt was made to establish the existence of the analogous $[M-O_6]^z$ system using one metal, Fe, and Clcat as the ligand. An eight-membered series can be envisaged with the two most reduced members formulated as Fe(II) plus three $Clcat^{2-}$ groups ($z = -4$) and Fe(III) plus three $Clcat^{2-}$ groups ($z = -3$). The most oxidized member could then be Fe(III) plus three $Clcat^0$ groups ($z = +3$). Evidence for the existence of this member in series with different ligands is afforded by the isolation of $FeCl_3 \cdot 3phenan$,[20] $FeBr_3 \cdot 3phenan$,[22] and $FeBr_3 \cdot 3chrysenequinone$.[22] The slight reduction of the carbonyl frequency in the second compound[22] might be indicative of the appropriateness of the $[Fe(phenan)_3]Br_3$ formulation; the magnetic moment of this compound[22] corresponds to the expected $S = {}^5/_2$ ground state.

Attempts to prepare pure samples of $FeCl_3 \cdot 3Clcat$ were unsuccessful. However, evidence for the existence of certain members of the $Fe(Clcat)_3^z$ series was obtained by chemical preparation of the purple anion $Fe(Clcat)_3^{3-}$ and observation of its oxidation–reduction behavior. This complex has a moment in agreement with a high-spin octahedral Fe(III) structure. In acetonitrile a one-electron reduction to the $z = -4$ species is observed at −1.66 v. In dichloromethane three well-developed one-electron oxidation waves are observed (*cf.* Table III), presumably corresponding to the formation of the $z = -2, -1, 0$ complexes. Attempted preparation of the neutral complex by reaction of $Fe(CO)_5$ with tetrachloro-*o*-quinone in 1:3 mole ratio in several inert solvents led to dark green crystalline products containing no carbon monoxide or quinone, but analyzing consistently 2% high in carbon for the $Fe(Clcat)_3^0$ formulation.

The limited results at hand are believed to support the plausibility of an $[M-O_6]^z$ series with M = Fe, although stabilization of all members with the same ligand system may not be possible. Chemical preparation of additional members is required for confirmation of the $[Fe-O_6]^z$ series. No further work is planned in this area.

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(51) Over voltage sweep ranges from 0.5 to 13 v sec^{-1} the anodic and cathodic peak currents were equal. The difference $|E_p - E_{p/2}|$ was *ca.* 65 mv, and the ratio of peak current to the square root of the sweep rate was independent of the sweep rate.

(52) D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961). It should be noted that α^2 values calculated from isotropic nuclear hyperfine splittings found for CuO_4 complexes are probably not reliable in a relative sense (*cf.* H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **43**, 1744 (1965)); however, reliable relative α^2 values do result from use of anisotropic hyperfine splittings (H. A. Kuska, private communication).

(53) G. J. Hoijtink, *Rec. Trav. Chim.*, **77**, 555 (1958).

(54) (a) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964); (b) G. N. Schrauzer and V. P. Mayweg, *Chem. Ind.* (London), 1464 (1965); (c) E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 4012 (1965).