Monatshefte für Chemie 111, 935—943 (1980)

Monatshefte für Chemie

Coordination of Zwitterionic 8-Quinolinol (Oxine) to Mixed Oxinate-Carboxylate Complexes of Divalent Nickel, Manganese, and Magnesium

M. M. Aly[a,*] and **A. M. Shalaby**[b]

[a] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt
[b] Chemistry Department, Faculty of Science, El-Mansoura University, El-Mansoura, Egypt

(Received 30 March 1978. Accepted 20 June 1978)

Three types of metal complexes containing coordinated zwitterionic 8-Quinolinol(oxine) are isolated from the reaction of MOx_2 (M = divalent Ni,Mn, or Mg; HOx = oxine) and haloacetic acids RCO_2H ($R = CF_3$, CCl_3, $CHCl_2$, or CH_2Cl) in benzene. These types are: $M(O_2CR)Ox \cdot HOx$ for M = Ni, $R = CCl_3$, $CHCl_2$, and CH_2Cl and for M = Mn, $R = CHCl_2$. $MOx(HOx)(RCO_2)MOx \cdot nH_2O$ for M = Ni, Mn, or Mg, $R = CF_3$ and n = 1,1, and 4, respectively. $MOx(HOx)(RCO_2)_2\,MOx$ for M = Mn and $R = CCl_3$. These types are compared with the simple mixed chelate $Mn(O_2CCH_2Cl)Ox$. Interrelated reactions are suggested to explain the formation of these metal complexes and the contributing factors are discussed. The coordination of the zwitterion to the metal ion through its phenolate oxygen and the presence of the triatomic system $^+N—H \ldots O$ in the three types of metal complexes are evidenced by typical infrared bands. Analytical and spectral data are in accordance with the suggested formulations.

(Keywords: Complexes, mixed; Magnesium complexes; Manganese complexes; Nickel complexes; Zwitterionic oxine, complexes)

Koordination von zwitterionischem 8-Chinolinol (Oxin) an gemischten Oxinat—Carboxylat-Komplexen des divalenten Nickel, Mangan und Magnesium

Drei Typen von Metallkomplexen mit koordiniertem zwitterionischem 8-Chinolinol (Oxin) wurden aus der Reaktion von MOx_2 [M = Ni(II),Mn(II),Mg(II); HOx = Oxin] mit Halogen-essigsäuren $RCOOH$ ($R = CF_3$, CCl_3, $CHCl_2$, CH_2Cl) in Benzol isoliert. Es werden Reaktionswege zur Bildung der Komplexe diskutiert. Die Koordination des Zwitterions über den phenolischen Sauerstoff und die Präsenz der Gruppierung $^+N—H \ldots O$ in allen Typen der untersuchten Metallkomplexe wird auf Grund typischer IR-Banden nachgewiesen.

0026-9247/80/0111/0935/$ 01.80

Introduction

The tendency of the metal oxinates to form adducts with the oxine ligand is a widely reported observation[1,2]. This type of metal complexes included the recently discussed $UO_2 \cdot Ox_2 \cdot HOx$ and $ThOx_4 \cdot HOx$ complexes (ref.[3] and [4]). Earlier suggestions[5,6] that the added oxine molecule in the U(VI) complex is an uncoordinated crystal lattice component were in contrary to those[7–9] assuming coordination to the U(VI) atom. X-Ray structural determination[10] and other investigations using ^{14}C-tracer and infrared techniques[4,11] proved that the oxine molecule added to the neutral U(VI) and Th(IV) oxinates is coordinated to the metal atom as a zwitterion through its phenolate oxygen. Solvent addition compounds and polymeric structures were recently suggested[12] for the interaction of the neutral Ni(II) oxinate complex with chloroform, methanol, dioxane and water.

The biological importance of mixed ligand complexes and their significance in toxicological processes prompted the investigation of some oxinate—carboxylate metal complexes.

Experimental

BDH chemicals were used. Metal oxinates were prepared as described before[2]. Solvents were spectra grade. The infrared measurements of metal complexes were obtained using a Perkin-Elmer 577 Grating Infracord (4,000-200 cm^{-1}). Solid samples were examined as nujol mulls. The electronic spectra were measured using a Unicam SP 8000 spectrophotometer. Chlorine analysis was performed at the analytical unit of the university of Assiut, while the carbon, hydrogen, nitrogen, and fluorine analyses were carried out at Dr. *F. B. Strauss* microanalytical laboratory. Standard methods were used for the determination of the metal content of the complexes. The isolated complexes were dried under vacuum over phosphorus pentoxide.

The reaction of the metal oxinates MOx_2 (M = divalent Ni, Mn, or Mg; HOx = oxine) and haloacetic acids RCOOH ($R = CF_3, CCl_3, CHCl_2$, and CH_2Cl) was carried out as follows. The powdered metal oxinate (0.006 mol) was added to the benzene solution (100 ml) of the acid (0.012 mol). The resulting solution was refluxed for 1 h. Dissolution of the Ni(II) oxinate took place before the precipitation of the product from the boiling solution. Similtaneous dissolution of the starting complex and precipitation of the product was observed in the cases of the Mn(II) and Mg(II) oxinates. The precipitated complex was filtered from the warm solution, washed with benzene and dried.

Results and Discussion

The four types of suggested formulations, shown in Scheme 1, are based on the analytical data (Tab. 1), vibrational spectra (Tab. 2) and electronic spectra (Tab. 3). These types were isolated from the reaction

Table 1. *Reference designations, suggested formulations, elemental analyses, colour, and effect of heat for the metal complexes.* (F_3, Cl_3, Cl_2, Cl refer to $R\mathrm{CO}_2^-$ with $R = \mathrm{CF}_3$, CCl_3, CHCl_2, and $\mathrm{CH}_2\mathrm{Cl}$ respectively)

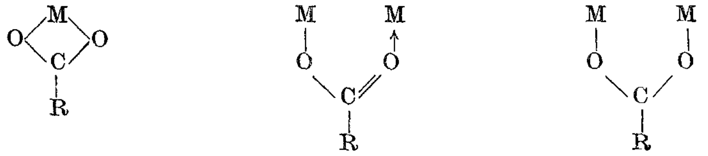
Ref. Design.	Suggested Formulations C = Calculated, F = Found	Elemental Analyses (%)					Colour	Effect of heat (°C)
		C	H	N	Halogen	metal		
I	$\mathrm{Ni}Ox(\mathrm{H}Ox)(\mathrm{F}_3)\mathrm{Ni}Ox\cdot\mathrm{H}_2\mathrm{O}$ $\mathrm{C}_{29}\mathrm{H}_{21}\mathrm{N}_3\mathrm{F}_3\mathrm{O}_6\mathrm{Ni}_2$	(C) 51.08 (F) 51.36	3.10 3.15	6.16 6.32	8.36 8.03	17.22 17.26	green	melting at 245
II	$\mathrm{Mn}Ox(\mathrm{H}Ox)(\mathrm{F}_3)\mathrm{Mn}Ox\cdot\mathrm{H}_2\mathrm{O}$ $\mathrm{C}_{29}\mathrm{H}_{21}\mathrm{N}_3\mathrm{F}_3\mathrm{O}_6\mathrm{Mn}_2$	(C) 51.65 (F) 51.40	3.14 3.22	6.23 6.01	8.45 8.29	16.26 16.17	buff- yellow	changes to brown at 290
III	$\mathrm{Mg}Ox(\mathrm{H}Ox)(\mathrm{F}_3)\mathrm{Mg}Ox\cdot 4\,\mathrm{H}_2\mathrm{O}$ $\mathrm{C}_{29}\mathrm{H}_{27}\mathrm{N}_3\mathrm{F}_3\mathrm{O}_9\mathrm{Mg}_2$	(C) 52.21 (F) 52.28	2.87 3.02	6.30 6.21	8.54 8.37	7.29 7.41	yellow	changes to brown at 305
IV	$\mathrm{Ni}Ox(\mathrm{H}Ox)(\mathrm{Cl}_3)$ $\mathrm{C}_{20}\mathrm{H}_{13}\mathrm{N}_2\mathrm{Cl}_3\mathrm{O}_4\mathrm{Ni}$	(C) 47.06 (F) 47.31	2.57 2.72	5.49 5.60	20.84 20.67	11.50 11.76	green	changes to black at 190
V	$\mathrm{Mn}Ox(\mathrm{H}Ox)(\mathrm{Cl}_3)_2\mathrm{Mn}Ox$ $\mathrm{C}_{31}\mathrm{H}_{19}\mathrm{N}_3\mathrm{Cl}_6\mathrm{O}_7\mathrm{Mn}_2$	(C) 42.29 (F) 42.43	2.21 2.38	4.84 5.03	24.51 24.68	12.66 12.43	buff- yellow	changes to black at 230
VI	$\mathrm{Ni}Ox(\mathrm{H}Ox)(\mathrm{Cl}_2)$ $\mathrm{C}_{20}\mathrm{H}_{14}\mathrm{N}_2\mathrm{Cl}_2\mathrm{O}_4\mathrm{Ni}$	(C) 50.47 (F) 50.71	2.96 3.05	5.89 5.71	14.90 15.04	12.33 12.49	green	changes to brown at 260
VII	$\mathrm{Mn}Ox(\mathrm{H}Ox)(\mathrm{Cl}_2)$ $\mathrm{C}_{20}\mathrm{H}_{14}\mathrm{N}_2\mathrm{Cl}_2\mathrm{O}_4\mathrm{Mn}$	(C) 50.87 (F) 50.61	2.99 3.12	5.93 5.72	15.02 15.30	11.63 11.85	buff- yellow	melting art 200
VIII	$\mathrm{Ni}Ox(\mathrm{H}Ox)(\mathrm{Cl})$ $\mathrm{C}_{20}\mathrm{H}_{15}\mathrm{N}_2\mathrm{ClO}_4\mathrm{Ni}$	(C) 54.41 (F) 54.24	3.42 3.31	6.34 6.49	8.03 8.15	13.30 13.16	greenish yellow	changes to brown at 260
IX	$\mathrm{Mn}Ox(\mathrm{Cl})$ $\mathrm{C}_{11}\mathrm{H}_8\mathrm{NClO}_3\mathrm{Mn}$	(C) 45.16 (F) 45.32	2.76 2.90	4.79 4.71	12.12 12.38	18.78 18.65	buff- yellow	melting at 210

Table 2. *Infrared spectra (cm^{-1}) of metal complexes (nujol mull, see Tab. 1 for reference designations)*

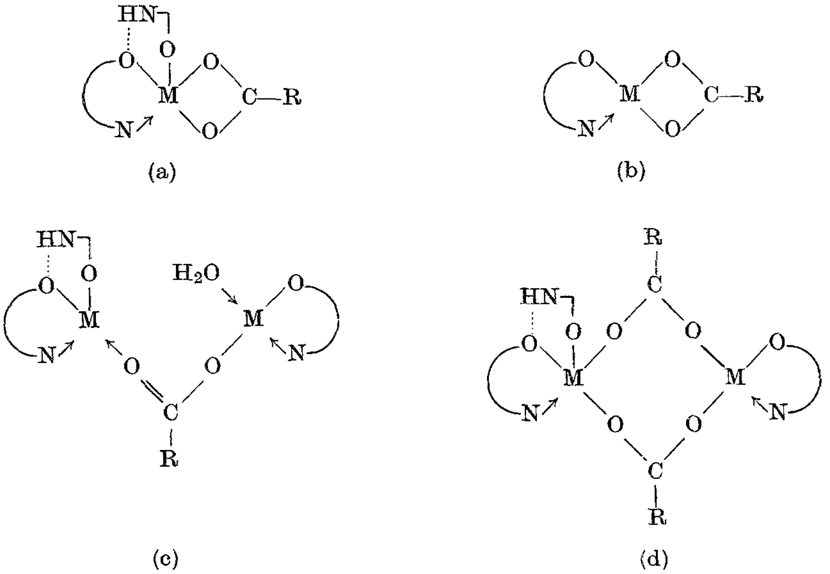
I	II	III	IV	V	VI	VII	VIII	IX	Band assignement
1675 (s)	1670 (s)	1710 (m)	1655 (m)	1668 (s)	1628 (s)	1638 (s)	1605 (s)	1603 (s)	ν_{as} of carboxylate
1378 (m)	1350 (m)	1355 (m)	1366 (m)	1385 (s)	1392 (m)	1383 (m)	1404 (m)	1404 (m)	ν_s of carboxylate
1117 (s) 1108 (s)	1113 (s) 1108 (s)	1118 (m) 1112 (m)	1117 (s) 1107 (s)	1113 (m) 1106 (s)	1112 (s) 1103 (m)	1112 (s) 1103 (s)	1119 (s) 1103 (m)	1112 (s)	ν C—O of oxinate ref.[13]
545 (s) 522 (m) 498 (m)	522 (w) 502 (s)	522 (w) 515 (m) 503 (m)	513 (m) 503 (m)	514 (m) 504 (s) 498 (m)	504 (s)	508 (m) 500 (s) 498 (m)	540 (w) 513 (m) 506 (s)	500 (s)	in-plane C—O bend ref.[14]
443 (m)	438 (m) 403 (m)	435 (w)	443 (m)	445 (m)	412 (m)	422 (w)	410 (s)	420 (w)	chelate ring def.
410 (w)	398 (m)	413 (m)	413 (m)	403 (m)	403 (m)	406 (w)	405 (s)	404 (m)	ref.[15]
308 (w) 295 (m) 285 (m)	288 (w) 268 (m)	268 (w)	293 (w) 275 (w)	282 (w)	300 (w) 288 (m) 268 (m)	270 (m)	385 (m) 368 (m)	282 (w) 260 (m)	M—O vibrations ref.[15]
242 (s) 230 (m)	240 (s)	230 (m)	238 (s)	242 (m)	240 (w)	242 (m) 232 (w)	245 (m)	240 (m) 228 (m)	M—X vibrations ref.[15]

of the haloacetic acid (HA) with the metal oxinate (MOx_2). The general formulations of these types are as follows:

Scheme 1



symmetrical chelating unsymmetrical bridging symmetrical bridging



(a) $MOxA \cdot HOx$, compounds IV, VI, VII, and VIII;
(b) $MOxA$, compound IX;
(c) $MOx(HOx)AMOx \cdot n H_2O$, compounds I, II, and III; and
(d) $MOx(HOx)A_2MOx$, compounds V.

The formation of type (a) follows reaction (1).

$$MOx_2 + HA \rightarrow MOxA \cdot HOx \qquad (1)$$

This reaction involves the cleavage of the M—N bond of a coordinated oxinate followed by the protonation of the nitrogen atom. In such a case the formed zwitterion oxine molecule will be coordinated via the phenolate oxygen and the haloacetate anion will be simultaneously coordinated to the metal ion. Hydrogen bonding formation that combines the $^+N—H$ of the monodentate oxine and an oxygen atom of either the carboxylate or the bidentate oxinate would produce the triatomic system $^+N—H \ldots O$. This argument is supported by the close similarity of the broad band centered between 2,500-2,400 cm^{-1} and the weak band near 2,050 cm^{-1} which were observed for these compounds in comparison with those cited as an evidence for the $^+N—H \ldots O$ system in the oxine adduct of U(VI)[3] and Th(IV)[4] oxinate. These bands were observed only from concentrated mulls, a behaviour which was similarly reported in ref.[3,4]. Furthermore, the splitting of the reproducible and previously assigned 1,100 cm^{-1} band (νC—O of the coordinated oxinate[13]) to two bands, separated by 10-16 cm^{-1}, is compatible with the formulation of type (a) metal complexes with two types of coordinated oxinate; a bidentate oxinate and a monodentate zwitterion. The splitting observation of the νC—O band was not observed for compound IX [type (b)], the suggested formulation of which is a bidentate oxinate and a bidentate carboxylate coordinated to the Mn(II) ion; see Tab. 2. This observation is in accordance with the proposed dissimilarity in the coordination of the two oxinate to the metal in compounds IV, VI, VII and VIII. The shift of the positions of the in-plane (C—O) bending, chelate ring deformation and metal—ligand vibrations from their positions[14, 15] in the metal oxinates to those listed in Tab. 2 of the mixed ligand complexes is ascribed to the characteristic vibrations associated with these structures. Bidentate

Table 3. *Electronic spectra of metal complexes in* $CHCl_3$ *(see Tab. 1 for reference designations)*

Ref. Design.	Absorption maxima* (nm)
I	365, 330, 255 (a)
II	370, 315, 255 (a)
III	365, 315, 250 (a)
IV	365 (3 660), 332 (4 390), 245 (4 290)
V	368 (1 510), 310 (2 880), 252 (13 500)
VI	nujol mull 385 (sh), (b)
VII	367, 313, 250 (a)
VIII	365, 335, 252 (a)
IX	385, 330, 315, 253 (a)

---

* The values in parentheses are the molar absorptivities (l mole^{-1} cm^{-1}).

(a) Partially soluble in chloroform (0.03 g in 25 ml solvent).

(b) Completely insoluble is chloroform.

coordination of the carboxylate to the metal atom is suggested in these compounds similar to other haloacetate complexes[16]. The vibrational bands characterizing ν_{as} and ν_s of the carboxylate are shown in Tab. 2. The reported[17, 18] sensitivity of the stretching vibrations relating to the bidentate carboxylate to both the substitution in the acetate anion and the nature of the coordinated metal ion resulted in the listed frequencies in Tab. 2 for ν_{as} and ν_s.

Reactions (2), (3) and (4) are suggested to explain the formation of types (b), (c), and (d) metal complexes.

$$MOx_2 + \mathrm{H}A \rightarrow [MOx]^+ [Ox\mathrm{H}A]^- \rightarrow MOxA + \mathrm{H}Ox \qquad (2)$$

$$MOxA(\mathrm{H}Ox) + [MOx]^+ \rightarrow MOx(\mathrm{H}Ox)AMOx \qquad (3)$$

$$MOx(\mathrm{H}Ox)AMOx + [Ox\mathrm{H}A]^- \rightarrow MOx(\mathrm{H}Ox)A_2MOx + \mathrm{H}Ox \qquad (4)$$

The dissociation of the HOx molecule from the ion pair in reaction (2) produces the simple mixed chelate compound IX of type (b). The reactivity of the ion pair, suggested in the latter reaction, is decisive for the nature of the product. The factors that influence the stability of the ion pair [to give reaction (2)] and its reactivity in reaction (1) [required for reactions (3) and (4)] could be (i) the stability constant of the metal oxinate itself[19] where the order of the stability constant is Cu > Co > Ni > Mn > Zn > Mg, (ii) the pK of the haloacetic acid (iii) the stability of the product obtained from the reaction step under consideration.

Reaction (3) illustrates the reactivity of the ion pair with the product of reaction (1) to give a type (c) metal complex. This type includes compounds I, II, and III obtained from the reaction of trifluoroacetic acid with the corresponding divalent metal oxinate. Further reaction of the ion pair with the product of reaction (3) constitutes reaction (4), the product of which is represented by compound V; type (d) metal complex. This compound was isolated from the reaction of trichloroacetic acid with Mn(II) oxinate. The relationship between reactions (3) and (4) suggests the coexistence of both products of type (c) and (d) metal complexes respectively. The solubility differences hampered the isolation of both types of metal complexes except in the case of Co(II) where the 1 h reaction gave the type (c) metal complex while the 24 h reaction (in the presence of excess trifluoroacetic acid) produced a type (d) metal complex[20].

While the symmetrical bidentate chelation of the carboxylate is suggested for types (a) and (b) metal complexes, bridging of the carboxylate, however, appears to satisfy the structural requirements of the metal complexes of types (c) and (d). The proposed coordination of the carboxylate and structural formulations of the four types of metal complexes are displayed in Scheme 1.

Evidence for the coordination of the zwitterion oxine molecule in types (c) and (d) metal complexes through its phenolate oxygen and the subsequent formation of the triatomic $^+$N—H ... O system are similar to those discussed above for type (a) metal complexes (Tab. 2). The observed shift of the broad band at 2,500-2,400 cm^{-1} from that reported[3,4] at 2,650 cm^{-1} which was assigned to the same $^+$N—H ... O system in $UO_2Ox_2 \cdot HOx$ and $ThOx_4 \cdot HOx$ is explained by stability differences. The presence of the coordinated water molecule in type (c) metal complexes is shown by the broad band at 3,500-3,300 cm^{-1} of the ν O—H of the probably hydrogen bonded water molecule. The deformation vibration and the band associated with the coordinated water molecule at the 1,000-800 cm^{-1} region[21] could not be assigned with certainty owing to their mixing with the oxinate and carboxylate vibrations.

The electronic spectra of the metal complexes are shown in Tab. 3. A profound difference between the spectrum of the metal oxinate and that of the corresponding mixed ligand complex is observed in the case of the Ni(II) complexes. Thus, the disappearance of the 460 nm peak of the Ni(II) oxinate and its substitution by a peak at 365 nm was observed for all Ni(II) complexes in Tab. 3. Similar disappearance of the 460 nm peak which is accompanied by the formation of another peak at 383 nm was recently reported[12] for the chloroform solution of Ni(II) oxiante containing methanol whereby a transformation from the tetrahedral structure of the Ni(II) oxinate to the distorted octahedral structure of the methanolic adduct is suggested. The electronic spectra of the Mn(II) complexes showed peaks which are regarded as resulting from the shift of the 396, and 335 nm peaks of the Mn(II) oxinate to lower frequencies[22]. The electronic spectrum of the Mg(II) complex is not significantly different from that of the metal oxinate[22]. These spectral observations are in accordance with the proposed structural formulations in Scheme 1. The absorption band around 250 nm in all metal complexes is ascribed to the coordinated carboxylate[23].

References

[1] *L. Pokras* and *P. M. Bernays*, J. Amer. Chem. Soc. **73**, 7 (1951); *S. Lenzer*, J. Chem. Soc. **1964**, 5768; *F. Hein* and *H. Regler*, Ber. **69**, 1692 (1936); *B. P. Block*, *J. C. Bailar*, and *D. W. Pearce*, J. Amer. Chem. Soc. **73**, 4971 (1951); *W. W. Wendlandt* and *J. H. Van Tassel*, Science **127**, 242 (1958).

[2] *R. G. W. Hollingshead*, Oxine and its Derivatives, Vol. II. London: Butterworths. 1954.

[3] *A. Corsini*, *J. Abraham*, and *M. Thompson*, Talanta **18**, 481 (1971); *A. Corsini* and *J. Abraham*, Canad. J. Chem. **48**, 2360 (1970).

[4] *J. Abraham* and *A. Corsini*, Anal. Chem. **42**, 1528 (1970).

[5] *T. Moeller* and *M. V. Rammaniah*, J. Amer. Chem. Soc. **76**, 5251 (1954).

[6] *J. H. Van Tassel* and *W. W. Wendlandt*, Ibid. **81**, 813 (1959).

[7] *E. P. Bullwinkel* and *P. Noble*, Ibid. **80**, 2955 (1958).

[8] *J. H. Van Tassel*, *W. W. Wendlandt*, and *E. Sturm*, Ibid. **83**, 810 (1961).

[9] *B. C. Baker* and *D. T. Sawyer*, Inorg. Chem. **8**, 1160 (1969).

[10] *D. Hall*, *A. D. Rae*, and *T. W. Waters*, Acta Cryst. **22**, 258 (1967).

[11] *A. Corsini* and *J. Abraham*, Chem. Commun. **1967**, 1101.

[12] *E. Sekido* and *K. Kunikida*, Analyt. Chim. Acta. **92**, 183 (1977).

[13] *R. G. Charles*, *H. Freiser*, *R. Friedel*, *L. E. Hilliard*, and *W. D. Johnston*, Spectrochim. Acta **8**, 1 (1956).

[14] *J. E. Tackett* and *D. T. Sawyer*, Inorg. Chem. **3**, 692 (1964).

[15] *N. Ohkaku* and *K. Nakamoto*, Ibid. **10**, 798 (1971).

[16] *A. B. P. Lever* and *D. Ogden*, J. Chem. Soc. **1967**, 2041.

[17] *A. V. R. Warrier* and *P. S. Narayanan*, Spectrochim. Acta **23 A**, 1061 (1967).

[18] *A. V. R. Warrier* and *R. S. Krishnan*, Spectrochim. Acta **27 A**, 1243 (1971).

[19] *J. Bjerrum*, *G. Schwarzenbach*, and *L. G. Sillen*, Stability Constants, Part I, Organic ligands, (Special Publication No. 6). London: The Chemical Society. 1957.

[20] *M. M. Aly* and *A. M. Shalaby*, in preparation.

[21] *J. Fujita*, *K. Nakamoto*, and *M. Kobayashi*, J. Amer. Chem. Soc. **78**, 3963 (1956).

[22] *K. Sone*, J. Amer. Chem. Soc. **75**, 5207 (1953).

[23] *M. Kato*, *H. B. Jonassen*, and *J. C. Fanning*, Chem. Rev. **64**, 99 (1964).