Articles

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vic-Dioximate Complexes of Silver(III)

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Bis chelate complexes of trivalent silver with several vic-dioximate ligands [dimethylglyoximate (dmg), diphenylglyoximate (dpg), cyclohexane-1,2-dione dioximate (chdd)] have been prepared by direct mixing of $Ag(OH)_4^-$ and the ligands in alkaline solutions. These complexes are intensely colored with two ligand-to-metal charge-transfer bands at 440–470 and 556–586 nm. They undergo internal redox within several minutes with the order of stability chdd > dmg > dpg. They appear to gain maximum stability by attaining a pseudomacrocyclic structure via outside protonation. The dmg complex has an overall formation constant of 1.6×10^8 M^{-2} at 10 °C and in 1.2 M NaOH. Formation and decomposition kinetics have been studied for the dmg complex and are interpreted in terms of stepwise chelation followed by intramolecular electron transfer in the bis and (less stable) mono complexes as well as destabilization of the +3 oxidation state by axial attack of a third ligand.

Introduction

Silver(III), with a d^8 electronic configuration, forms only a limited number of stable compounds because of the inaccessibility of a suitable ligand framework to coordinatively bind the unusual, higher valent central metal while, at the same time, resisting intramolecular electron transfer.[2] The known and well-characterized Ag(III) compounds include the mixed-valent AgO^3 and Ag_3O_4,[4a] the stoichiometric Ag_2O_3,[4b] the paramagnetic and octahedral M_3AgF_6,[5] and complexes derived from periodate and tellurate,[6] tetraazamacrocycles,[7] porphyrins,[8] biguanides,[9] phosphines and arsines,[10] polypeptides,[11] and hydroxo[6] and other oxo anions.[12] Transient silver(III) species involving $S_2O_3^{2-}$ [13] and N_3^- [14] are produced by the substitution of OH^- groups in $Ag(OH)_4^-$ prior to redox.

Dioximes are good ligands for the stabilization of higher oxidation states of transition metals because of their π-donor character[15] and form complexes of higher valent metals such as Cu(III),[16] Ni(III),[15,17,18] and Ni(IV).[15,17,18] It has been generally noted that ligands of the oxime–imine type[15,18] are mainly effective in aqueous acidic solutions and require one oxime function per metal for each unit increase in the oxidation state of the central metal and can therefore raise the oxidation state by one and/or two units.[15,18] On the other hand, the vic-dioximates, effective in alkaline solutions, are ligands that are especially and conveniently suited to raising the metal oxidation state by two units because of the proximity and the presence of two oximate functions attached to a π-system.[19] Thus, the dimethylglyoximate dianion (dmg^{2-}) may be used to prepare a stable complex of Ni(IV) ($3d^6$), tris(dimethylglyoximato)nickelate(IV), $Ni(dmg)_3^{2-}$,[19] free from contamination by the Ni(III) analogue.[20]

The present work was undertaken to gain insight into the formation and stability of vic-dioximate complexes of trivalent silver and to make comparisons with other such systems. We report here on attempts to prepare the silver(III) complexes by oxidation of univalent silver and on the direct reaction between these ligands and the $Ag(OH)_4^-$ ion. Complexes of limited stability have been observed with dimethylglyoxime, dmg (we use the abbreviation as a general term here; specific ionic charges and degrees of protonation are indicated where appropriate), diphenylglyoxime, dpg, and cyclohexane-1,2-dione dioxime, chdd.

Experimental Section

Materials. The reagents used were of analytical grade. Solutions of tetrahydroxoargentate(III), $Ag(OH)_4^-$, were prepared in 1.2 M NaOH by electrolysis of a silver-foil anode; the procedure was as previously described[6] except that the platinum-wire cathode was replaced by a silver foil, the larger surface area of the cathode eliminating possible problems associated with localized gas evolution. NaOH solutions were prepared fresh by using a sample of Fisher NaOH (50% w/w, 0.05% Na_2CO_3) and making appropriate dilution using freshly prepared doubly distilled water.

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(2) (a) McMillan, J. A. *Chem. Rev.* **1962**, *62*, 65. (b) Po, H. N. *Coord. Chem. Rev.* **1976**, *20*, 171. (c) Levason, W.; Spicer, N. D. *Coord. Chem. Rev.* **1987**, *76*, 45.
(3) (a) Dirkse, T. P. *J. Electrochem. Soc.* **1959**, *106*, 453. (b) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 167.
(4) (a) Standke, B.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 77. (b) Standke, B.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 188.
(5) Allen, G. C.; Warren, K. D. *Inorg. Chem.* **1969**, *8*, 1895.
(6) (a) Kirschenbaum, L. J.; Ambrus, J. H.; Atkinson, G. *Inorg. Chem.* **1973**, *12*, 2832. (b) Cohen, G. L.; Atkinson, G. *J. Electrochem. Soc.* **1968**, *115*, 1236.
(7) (a) Barefield, E. K.; Mocella, M. T. *Inorg. Chem.* **1973**, *12*, 2829. (b) Clark, I. H.; Harrowfield, J. MacB. *Inorg. Chem.* **1984**, *23*, 3740. (c) Pesavento, M.; Profumo, A.; Soldi, T.; Fabbrizzi, L. *Inorg. Chem.* **1985**, *24*, 3873.
(8) (a) Krishnamurthy, M. *Inorg. Chem.* **1978**, *17*, 2242. (b) Krishnamurthy, M.; Sutter, J. *Inorg. Chem.* **1985**, *24*, 1943. (c) Langley, P.; Hambright, P.; Williams, R. F. X. *Inorg. Chim. Acta* **1985**, *104*, L25. (d) Antipas, A.; Dolphin, D.; Goutermann, M.; Johnson, E. C. *J. Am. Chem. Soc.* **1978**, *100*, 7705. (e) Karwiek, D. H.; Winograd, N. *Inorg. Chem.* **1976**, *15*, 2336. (f) Kadish, K. M.; Davis, D. G.; Fuhrhop, J. H. *Angew Chem., Int. Ed. Engl.* **1972**, *84*, 1072. (g) *J. Am. Chem. Soc.* **1973**, *95*, 5140. (h) Po, H. N. *Inorg. Chim. Acta* **1978**, *31*, L421. (i) Kumar, A.; Neta, P. *J. Phys. Chem.* **1981**, *85*, 2830. (j) Bruhn, H.; Nigam, S.; Holzwarth, H. F. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 129.
(9) (a) Sen, D. N.; Ghosh, N. N.; Ray, P. *J. Indian Chem. Soc.* **1950**, *27*, 619. (b) Sen, D. *J. Chem. Soc. A* **1969**, 1307. (c) Chakravorty, B. *J. Inorg. Nucl. Chem.* **1979**, *41*, 757. (d) Banerjee, A. K.; Ghosh, S. P. *J. Indian Chem. Soc.* **1976**, *53*, 719. (e) Saha, C. R. *J. Inorg. Chem. Soc.* **1976**, *38*, 1635. (f) Sanyal, R. M.; Ansari, B. H.; Srivastava, P. C.; Banerjee, B. K.; Chakraburty, A. K. *Fert. Technol.* **1979**, *16*, 36.
(10) (a) Warren, L. F.; Bennett, M. A. *J. Am. Chem. Soc.* **1974**, *96*, 3340. (b) *Inorg. Chem.* **1976**, *15*, 3126.
(11) Kirschenbaum, L. J.; Rush, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 1003.
(12) Rush, J. D.; Kirschenbaum, L. J. *Polyhedron* **1985**, *4*, 1573.
(13) Rush, J. D.; Kirschenbaum, L. J. *Inorg. Chem.* **1985**, *24*, 744.
(14) Borish, E. T.; Kirschenbaum, L. J. *Inorg. Chem.* **1984**, *23*, 2355.

(15) (a) Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1. (b) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *31*, 87.
(16) (a) Sulfab, Y.; Al-Shatti, N. I. *Inorg. Chim. Acta* **1984**, *87*, L23. (b) Morpurgo, G. O.; Tomlinson, A. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 744. (c) Datta, D.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 1611. (d) Butcher, R. J.; O'Connor, C. J.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 537.
(17) (a) Baucom, E. I.; Drago, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 6469. (b) Drago, R. S.; Baucom, E. I. *Inorg. Chem.* **1972**, *11*, 2064.
(18) Singh, A. N.; Singh, R. P.; Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1977**, *16*, 2597.
(19) (a) Panda, R. K.; Acharya, S.; Neogi, G.; Ramaswamy, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1225. (b) Neogi, G.; Acharya, S.; Panda, R. K.; Ramaswamy, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1233.
(20) Baral, S.; Lappin, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 2213.

Solutions of the dioximate ligands were also freshly prepared before use by dissolving reagent grade samples of dimethylglyoxime, H_2dmg (Matheson), diphenylglyoxime, H_2dpg, (benzil α-dioxime; Hopkin and Williams), α-furil dioxime, H_2fd (Sigma), and cyclohexane-1,2-dione dioxime, H_2chdd (Nioxime; Koch-Light) in low-carbonate hydroxide solutions of desired alkalinity. The concentration of the $Ag(OH)_4^-$ was determined from the UV-visible spectrum [$\epsilon_{max(267)}$ of $Ag(OH)_4^- = 1.17 \times 10^4$ M^{-1} cm^{-1} in aqueous alkaline solutions[6]].

Preparation of Dioximate Complexes of Silver(III). (a) By the Direct Reaction of $Ag(OH)_4^-$ with Dioximate Ions. An ice-cold solution of $Ag(OH)_4^-$ in base was added to a cold and weakly basic solution of the dioximate ligand(s) (L). Maximum stability resulted when $[L]_0$ was 5-10 times $[Ag(OH)_4^-]_0$ and the pH of the reaction mixture was 12-13. While addition of dmg, dpg, and chdd resulted in the formation of deeply colored complexes (vide infra), basic solutions of fd did not form any noticeable complex, either because of simultaneous decomposition or a lack of significant formation. Under identical conditions the relative kinetic stability of the complexes with the different ligands was chdd > dmg > dpg. Precipitation with tetraethylammonium ion resulted in deeply colored solid complexes, but self-decomposition prevented isolation of the pure solids.

(b) By the Reaction of Dioximate Solutions with AgO. The mixed-valent silver oxide AgO (which contains Ag(I) and Ag(III) with a formulation $Ag^IAg^{III}O_2$) was prepared[3] and placed in a sintered tube of medium porosity. When a basic solution of dmg was drawn through the tube, the filtrate turned a deep red, indicative of the Ag(III)-dmg complex.

Attempts to prepare the dioximate complexes of higher valent silver by peroxodisulfate oxidation of the Ag(I)-dioximate complex Ag-$(dmgH)_2^-$ resulted in ligand oxidation only.

Spectra. UV-visible spectra were recorded either on a Cary 15 or a Beckman DU7 spectrophotometer. Because of the high background absorbance of concentrated NaOH, reliable measurements below 230 nm could not be made. IR spectra were obtained for KBr disks on a Perkin-Elmer 281B grating instrument. EPR spectra of frozen solutions of the complex were taken on a Bruker ER 220D-LR ESR spectrometer with an ER 4111 VT variable-temperature system at 123 K. The spectra were devoid of any signal, showing that all the complexes are diamagnetic.

Spectrophotometric Titrations. Equal volumes of $Ag(OH)_4^-$ and dmg were rapidly mixed (at 10 °C, $\mu = [OH^-] = 1.2$ M) in the stopped-flow apparatus. Several concentration ratios, $[dmg]_0/[Ag(OH)_4^-]_0 = 1$-20, were employed for this purpose. The reduced temperature allowed the accurate determination of total [Ag(III)] (at 267 nm) as well as the absorbance of equilibrium amounts of complex at higher λ.

Decomposition Products. The dioximate complexes of silver(III) were found to undergo self-decomposition forming $Ag(OH)_2^-$, the liberated free ligand, and an oxidized product of the ligand. In a typical experiment involving the dmg complex, the products were qualitatively analyzed as follows. In a total volume of 500 mL containing $[Ag(OH)_4^-]_0 \sim 1 \times 10^{-3}$ M, $[dmg]_0 = 4 \times 10^{-3}$ M, and $[OH^-] = 1.2$ M, the deep red solution was allowed to stand for enough time to ensure complete decomposition. The reaction mixture was neutralized in pH ~ 7 with $HClO_4$, and a calculated excess of Ni(II) solution was added to precipitate all the dioxime as the scarlet red $Ni(dmgH)_2$, which was filtered out, dried, and characterized. The solution containing Ag(I) was treated with $HClO_4$ (pH < 1) and repeatedly extracted with diethyl ether, and the ether extract was collected. The extract was thoroughly washed with small portions of dilute solutions of Ni(II), NH_4OH, and finally with water, and the ether layer was collected and dried over anhydrous Na_2SO_4. The ether was slowly removed while cold, and the resulting red-brown product was collected. It was recrystallized from acetone and vacuum-dried overnight, and its IR spectrum was taken. The important bands[21] were (all cm^{-1}): 3200 (br, ν_{O-H}), 2915 (s, ν_{CH_3}), 1685 (s, $\nu_{C=N}$), 1440 (ν_{asCH_3}), 1382 (m, ν_{C-H}), 1365, 1310 (s, ν_{O-N-O}), 1138, 1120 (s, ν_{N-O-H}), 978, 902, 740 (ν_{N-O}), 702, 610 (m, $\nu_{C=N-O}$ bend). The spectrum was identified as that of 1-(hydroxyimino)-2-nitrobutane (IA), which

$$\text{IA} \qquad\qquad \text{IB}$$

may be formed during the isolation procedure via acid hydrolysis of 3,4-dimethyl-fur-2,5-azan N-oxide (IB). Although uncertainties in silver

(21) Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden-Day and Nankodo Co.: Tokyo, 1966; Chapter 2.
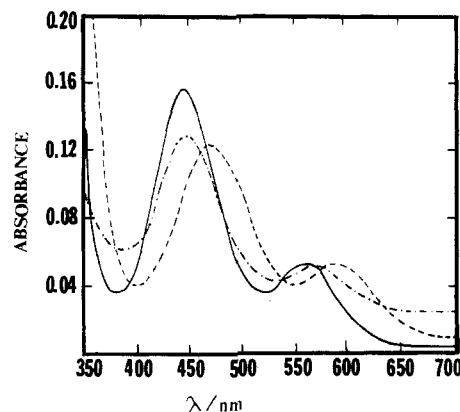
Figure 1. Visible spectra of silver(III) *vic*-dioxime complexes. Ligands: (—) dmg; (---) dpg; (-·-) chdd. The total concentration of complex was about 1×10^{-5} M (1-cm cell), but it decreased somewhat during the time required for recording, especially for dpg. See text for determination of extinction coefficients.

Table I. Spectral Characteristics of $Ag(OH)_4^-$, *vic*-Dioximates, and the Dioximate Complexes of Silver(III)

species	λ_{max}, nm (log ϵ)		origin of transition
$Ag(OH)_4^-$		267 (4.07)	a
$dmgH_2$		225 (4.02)	b
dmg^{2-}		265 (4.27)	b
$dmgH^-$	218 (4.21)	265 (4.27)	c
$Ag(dmg)_2(H)_2^+$		~ 265	d
	442 (4.06)	556 (3.55)	e
dpg^{2-}		~ 273 (4.17)	b
$Ag(dpg)_2(H)_2^+$		273	d
	466 (3.92)	586 (3.54)	e
$chdd^{2-}$		265 (3.99)	b
$Ag(chdd)_2(H)_2^+$		263 (4.29)	d
	477 (3.93)	567 (3.31)	e
fd^{2-}		270 (4.35)	b, f

[a] Charge transfer. [b] $\pi \rightarrow \pi^*$. [c] $\pi \rightarrow \pi^*$ (asymmetric split). [d] $\pi \rightarrow \pi^*$ in the coordinated ligand. [e] LMCT. [f] No silver(III) complex formed.

concentration and loss of product during isolation preclude quantitative measurement of the redox stoichiometry, we may conclude that as in the reactions of dmg with Ni(IV), $Fe(CN)_6^{3-}$, and MnO_2,[22] IB is the primary product of oxidation by Ag(III).

Kinetics. Kinetic experiments were performed by mixing equal volumes of the ligand (dmg) and $Ag(OH)_4^-$ solutions, maintained at appropriate temperature (25 ± 0.1 °C), alkalinity, and ionic strength (with $NaClO_4$), in an Aminco-Morrow stopped-flow assembly interfaced to a Tandy TRS-80 microcomputer through a Starbuck Data Co. A/D converter. Kinetics of formation (% transmittance decrease or absorbance increase) and decomposition (absorbance decrease) of the dmg complex of Ag(III) were monitored at 442 nm (a wavelength maximum of the complex) for most of the runs, but the observed rate parameters were essentially wavelength independent in the 350-560-nm range. Because of the high background absorbance of the ligand, it was not possible to follow the reaction at the $Ag(OH)_4^-$ maximum of 267 nm. The $[Ag(OH)_4^-]_0$ was limiting and held in the range 1×10^{-5}-1×10^{-4} M. The time scales of the formation and the decomposition reactions were well separated. The rate constants calculated for several replicates of the same run were reproducible to within ±5%.

Results and Discussion

Stoichiometry and Spectra. When basic solutions of $Ag(OH)_4^-$ and the dioximate(s) were mixed, there was a rapid formation of an intense color (red for dmg and yellow-brown for dpg and chdd) due to the formation of the Ag(III) complex of the corresponding ligand. Under identical conditions, the reactant solutions of $Ag(OH)_4^-$ and the free dioximates absorb very weakly

(22) (a) Boyer, J. H.; Toggweiler, U. *J. Am. Chem. Soc.* **1957**, *79*, 895. (b) Elderfield, R. C., Ed. *Heterocyclic Compounds*; Wiley: New York, 1961; pp 469-471. (c) Paton, R. M. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Potts, K. T., Eds.; Pergamon: New York, 1984; Vol. 6, Part 4B, Chapter 4.22.

Table II. Stoichiometry and Equilibrium Quotient for Ag(III)–dmg Complexation[a] (10 °C; [OH⁻] = μ = 1.2 M)

10^5[Ag(III)], M	10^4[dmg], M	A/A_{lim}	$10^{-8}\beta_2$(calcd), M⁻¹
8.0	5.0	0.93	1.2
	2.0	0.62	1.6
	1.0	0.31	1.7
	0.50	0.14	2.1
3.0	2.0	0.74	1.2
	1.0	0.43	1.3
	0.50	0.22	2.2

Average log β_2 = 8.1 ± 0.2

[a] Actual Ag(III) concentrations varied by about 20% within a series and were normalized as appropriate before averaging. ϵ_{442} was determined from the limiting absorbance (A_{lim}) at high [dmg]. A/A_{lim} was taken as the fraction of silver complexed. The calculated quotient, β, varied by a factor of 8 when a dmg₁ complex was assumed and by an order of magnitude or more for higher order complexes.

in the visible region. The visible spectra of the three complexes are given in Figure 1. The spectra were recorded immediately after mixing at ~5 °C so that decomposition of the dmg and chdd complexes was negligible. Table I compares UV–visible spectral characteristics of the complexes with those of Ag(OH)₄⁻ and the free ligands.

Spectrophotometric titrations were carried out for the dmg system in order to determine the stoichiometry of complex formation. Because of the instability of Ag(OH)₄⁻ and the complex, the experiments were performed at 10 °C and μ = [OH⁻] = 1.2 M. A good fit of the absorbance (at 442 nm) data was found for a presumed ratio of dmg:Ag(III) = 2:1. A value of log $\beta_{2(\text{app})}$ = 8.1 ± 0.2 ([OH⁻] = 1.2 M) and an extinction coefficient ϵ_{442} = (1.12 ± 0.04) × 10⁴ M⁻¹ cm⁻¹ were calculated[23] for the bis complex. Representative data are given in Table II. The consistency of the results indicate that the mono complex has a relatively low absorbance and/or stoichiometric significance under these conditions.

The spectra of all the Ag(III)–dioximate complexes in aqueous alkaline solutions exhibit three absorption maxima above 230 nm, the band positions marginally varying with different ligands. The positions of the UV bands are almost identical in the free ligands and in the complexes (although somewhat reduced in intensity) and can be assigned to $\pi \rightarrow \pi^*$ transitions.[19,24] The visible absorptions in the complexes may be assigned to ligand-to-metal charge transfer (LMCT) by analogy with other systems that show similar intensities. For example, a 460-nm LMCT band was observed in the pseudooctahedral Ni(dmg)₃²⁻, which has a nitrogen-donor coordination sphere only.[19] The LMCT bands of several other planar Ag(III)–N₄ ligand systems (e.g., polypeptides,[11] tetraazamacrocycles,[7] porphyrins,[8] biguanides[9]) also resemble those observed in the present systems. Moreover, in the case of transient Ag(OH)₃(N₃)⁻, where the azide ligand is coordinated to the metal through the donor nitrogen,[14] a band appeared in the visible that is similar in character to other CT bands observed for various N-donors. On the other hand, had the dioximate ligand been coordinated through O-donors, the spectra of the complexes and that of the original Ag(OH)₄⁻ would have been similar.[12,16b,24]

Burger et al.[24] have demonstrated the presence of bridging hydrogens, O–(H)–O, as a general feature of dioximate complexes. This geometry has been confirmed in a number of crystallographic determinations.[25] The electronic structures of the palladium(II) and platinum(II) complexes of dmg and glyoximate[26] have recently been presented. The hydrogen-bridged structures impart strength to the donor nitrogens by forming a pseudomacrocyclic environ-

(23) Irving, H. M.; Rossotti, H. S. *J. Chem. Soc.* **1953**, 3397; **1954**, 2904.
(24) Burger, L.; Ruff, I.; Ruff, F. *J. Inorg. Nucl. Chem.* **1965**, 27, 179.
(25) (a) Calleri, M.; Ferraris, G.; Viterbo, D. *Inorg. Chim. Acta* **1967**, 1, 297. (b) Calleri, M.; Ferraris, G.; Viterbo, D. *Acta Crystallogr., Sect. B* **1969**, 25, 2066. (c) Frasson, E.; Parattoni, C.; Zannetti, R. *Acta Crystallogr.* **1959**, 89, 2132.
(26) DiBella, S.; Casarin, M.; Fragata, I.; Granozzi, G.; Marks, T. J. *Inorg. Chem.* **1988**, 27, 3993.

Table III. Observed and Calculated Rate Parameters for the Formation of the Dimethylglyoximate Complex of Silver(III)[a,b]

[OH⁻], M	10^3[dmg], M	E_f, s⁻¹	E_s, s⁻¹	sum	sum(calcd)[c]
1.2	0.10	4.4	2.0	6.4	6.5
	0.20	6.6	2.3	8.9	8.8
	0.50	10.7	5.1	15.8	15.1
	1.0	17.0	8.0	25.0	24.4
	2.0	23.7	13.4	37	39
	5.0	39	20	59	67
	10.0	55	31	86	90
	20.0	72	40	112	109
	50	86	53	139	124
0.72	0.10	6.0	3.1	9.1	9.0
	0.20	7.1	5.6	12.7	13.3
	0.50	13.1	8.5	21.5	24.3
	1.0	30	14.3	44	38
	2.0	41.4	20.4	62	55
	5.0	52	25	77	77
	10	62	30	92	89
	20	70	38	108	97
	50	75	43	118	102
0.36	0.10	12.0	6.7	18.7	17.0
	0.20	17.0	10.4	27.4	26.2
	0.50	24.6	14.5	39	43
	1.0	32	19.1	51	56
	2.0	38	22	60	66
	5.0	41	27	68	74
	10	42	28	70	80
0.18	0.10	25.2	13.8	39	33
	0.20	29	19	48	44
	0.50	37	26	63	57
	1.0	36	30	66	62
	2.0	37	29	66	62
	5.0	36	31	67	68
	10	36	31	67	69
0.12	0.10	26	15	41	44
	0.20	34	23	57	53
	0.50	36	26	62	60
	1.0	36	26	62	62
	2.0	36	25	61	64
	5.0	36	27	63	65
	10	36	27	63	65

[a] μ = 1.2 M and 25 °C; dmg was always in large excess with 1 × 10⁻⁵ M < [Ag(OH)₄⁻]₀ < 1 × 10⁻⁴ M. [b] E_f and E_s are the observed faster and slower exponential rate parameters; sum = E_f + E_s. [c] Calculated from eq 1.

ment. Experimental constraints prevent us from making the IR and UV measurements necessary to confirm proton bridging on the (dilute) solutions of Ag(III) complexes in the presence of excess ligand. However, on the basis of stoichiometry, spectra, and (decomposition) kinetic experiments (vide infra), we conclude that the principal forms of the complexes in the present study have the planar, bridged structure shown in II.

II
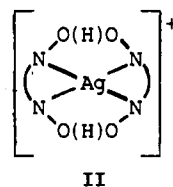
Formation Kinetics. The kinetics of the reaction between Ag(OH)₄⁻ and dmg were followed as complex formation at wavelengths above 350 nm. The disappearance of silver(III) could not be monitored accurately because of the high background absorbance of the ligand at lower wavelengths. The reaction kinetics are biphasic and were resolved into a sum of exponentials by either (i) nonlinear least-squares regression or (ii) determination of the smaller rate parameter, E_s, by a first-order analysis of the final portion of the reaction trace and the larger rate parameter, E_f, by a difference plot. The data are given in Table III. In neither case could a simple functional form be found, indicating that the two exponential terms are coupled. This situation most commonly arises from a sequential mechanism with reversible

steps. In such a case, the exponentials are solutions of a secular equation and contain contributions from all steps in the mechanism.[27] The sum of the rate parameters (sum $= E_f + E_s$) may be set equal to the sum of all (pseudo-first-order) rate constants, both forward and reverse. The product, $E_f \times E_s$, contains cross-terms,[27] which, because of concentration dependences for the various terms, can be rather complicated.

No satisfactory fit of the sum of rate parameters could be obtained that was a simple sum of concentration-dependent terms. Attempts were made to fit sum to a large variety of more complex functions by using nonlinear least-squares regression. A satisfactory result was obtained for the function given in eq 1. The

$$\text{sum} = C_1 + \frac{(C_2 + C_3[\text{OH}^-])[\text{dmg}]/[\text{OH}^-]^2}{1 + C_4[\text{dmg}]/[\text{OH}^-]^2} \quad (1)$$

final values of the four constants, when the relative errors for each measurement were minimized, are $C_1 = (4.21 \pm 0.47)$ s^{-1}, $C_2 = (1.37 \pm 0.12) \times 10^4$ s^{-1} M, $C_3 = (1.71 \pm 0.12) \times 10^4$ s^{-1}, and $C_4 = 256 \pm 20$ M. The results of this analysis are tabulated in Table III. The recalculated values of sum are well within expectations, with an average deviation of less than 7%. No function was found that gave a satisfactory fit for the product.
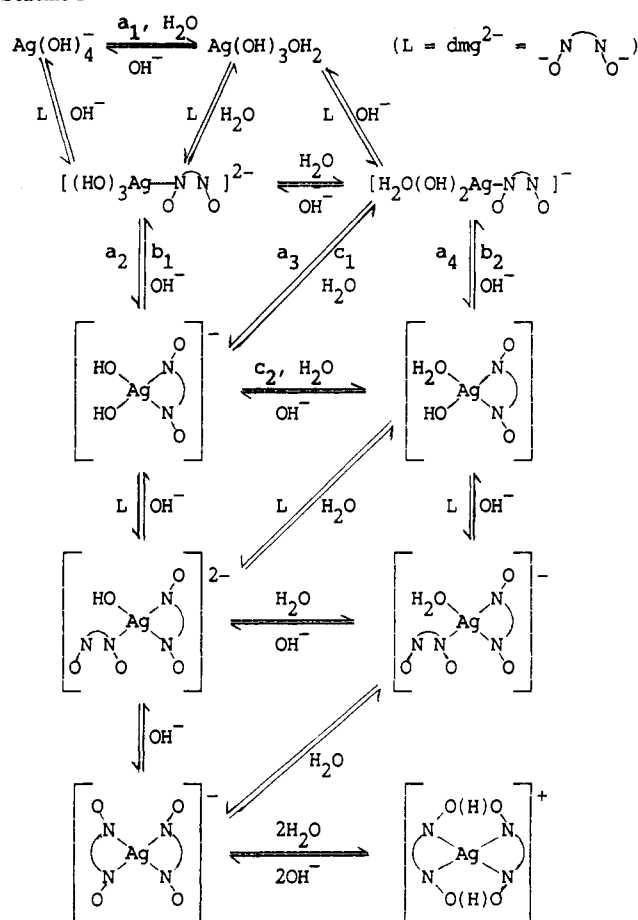
As suggested above, it seems clear that the formation mechanism of the bis(dimethylglyoximato)silver(III) complex involves a sequence of reversible steps. However, the form of eq 1 and our inability to analyze the product of rate parameters indicates that (i) two or more parallel paths involving different forms of silver(III) are important and/or (ii) there are more than two kinetically significant steps within a single path. Although we are unable to provide an unambiguous set of assignments, the discussion that follows represents our best interpretation of the rate data. We have verified the validity of our analysis, for several sets of rate constants and concentrations, by generating time vs concentration data with the Gear numerical integrator.[28]

A general mechanism for replacement of the four OH$^-$ groups by two bidentate ligands and two proton bridges is given in Scheme I. The four steps labeled a can contribute to the ligand-independent term, C_1, in eq 1. Step a_1 seems important in other Ag(OH)$_4^-$ reactions;[13] ring closing (a_2, a_3, a_4) seems important in the complexation of Ag(III) by tetraglycine.[11]

The presence of the denominator in eq 1 suggests that at least two rate constants and one equilibrium constant contribute to the second term. The [dmg]/[OH$^-$]^2 dependence in both numerator and denominator is most simply explained by reactions of [(OH)$_2$Ag(dmg)]$^-$ with a formation constant equal to 2.6 × 10^2 M ($= C_4$). In that case, C_3 most likely represents OH$^-$-promoted ring opening in the mono complex via one or both of the steps labeled b. The (perhaps composite) rate constant for this process would be $C_3/C_4 = 66$ s^{-1} M^{-1}. The hydroxyl-independent term, C_2, may be attributed to either the water-assisted ring opening (c_1) or hydrolysis of the mono complex (c_2) with a rate constant (or sum) of $C_2/C_4 = 53$ s^{-1}.

The foregoing analysis presumes that the rate-determining steps in the complexation reaction are all associated with the first chelation reaction. This seems reasonable in light of the absence of higher order terms in [dmg]. However, since a wavelength dependence was unable to distinguish intermediate species, and, in fact, a mixture of mono and bis complexes should be produced at low [dmg] and high [OH$^-$], other contributions cannot be ruled out. In addition, more than one kinetically equivalent step seems likely to contribute to some of the constants. Thus, in the absence of the ability to monitor Ag(OH)$_4^-$ disappearance or to detect the presence of intermediate stages of complexation or protonation (vide supra), we are unable to make unambiguous assignments of the formation rate data.

(27) (a) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; Chapter 8. (b) Lawani, S. A.; Sutter, J. R. *J. Phys. Chem.* **1973**, *77*, 1547. (c) Sutter, J. R.; Park, K. B. *J. Phys. Chem.* **1984**, *88*, 770.

(28) Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Prentice Hall: Englewood Cliffs, NJ, 1971.

Scheme I

Decomposition Kinetics. The Ag(III)–dioximate complexes decompose according to the overall reaction eq 2, where (L)$_{\text{ox}}$ is the product of intra- and/or intermolecular electron transfer. For

$$\text{Ag(L)}_2(\text{H})_2^+ + 2\text{OH}^- \rightarrow \text{Ag(OH)}_2^- + \text{L} + (\text{L})_{\text{ox}} \quad (2)$$

L = dmg, the product was identified as described above. The room-temperature stabilities of the Ag(III) complexes of the three dioximate ligands studied range from a few seconds to several minutes, depending on conditions, with the decomposition rate of each decreasing as [OH$^-$] decreases. The stability of the chdd complex is the highest (half-life of about 20 min at pH 11 compared to about 3 min for dmg and <1 min for dpg). We have chosen the dmg complex for a detailed mechanistic study.

The conditions employed for studying the decomposition reaction were those described in previous sections. In addition, several experiments were performed at lower [OH$^-$] in the pH range 10.70–11.55 (phosphate buffer) by a double mixing experiment in which solutions containing the Ag(III)–dmg complex were rapidly quenched with phosphoric acid and the 442-nm absorbance decrease was monitored. Quantitative experiments at pH < 10.7 were not possible because of the difficulty in getting [Ag(III)] high enough to form a significant concentration of the complex while the ionic strength was maintained at 1.2 M. We do note, however, that when the pH of the Ag(III)–dmg complex solution was brought down below pH = 10.7, it decomposed rapidly.

The decomposition of the Ag(III)–dmg complex obeys pseudo-do-first-order kinetics (observed rate constant k_d) for more than 4 half-lives. The experimental data are given in Table IV. The value of k_d exhibits a complex dependence on [dmg] and [OH$^-$] (Figure 2). As [dmg] increases from very low values, the value of k_d first becomes smaller and then increases. This latter trend is best demonstrated at higher base concentration where increased ligand solubility permitted experiments up to [dmg] = 0.05 M. Plots of k_d vs [OH$^-$] were generally concave upward with a common intercept of about 4.1 × 10^{-3} s^{-1}. Analysis of the data

Table IV. Pseudo-First-Order Constants (k_d) for the Decomposition of the Ag(III) Complex of Dimethylglyoxime[a]

[OH⁻], M	10³[dmg], M	10²k_d, s⁻¹	10²k_d(calcd), s⁻¹
1.2	0.1	7.3	6.8
	0.2	4.7	4.4
	0.5	3.3	2.9
	1.0	2.6	2.5
	2.0	2.3	2.4
	5.0	2.3	2.7
	10	3.7	3.3
	20	5.5	4.8
	50	8.4	9.0
1.0	10	2.6	2.6
0.72	0.1	2.5	3.1
	0.2	1.9	2.2
	0.5	1.6	1.7
	1.0	1.4	1.5
	2.0	1.4	1.5
	5.0	1.4	1.6
	10	1.9	1.8
	20	2.5	2.3
	50	3.8	3.9
0.55	10	1.5	1.4
0.36	0.1	1.6	1.3
	0.2	1.3	1.1
	0.5	1.1	1.0
	1.0	1.0	0.92
	2.0	0.97	0.91
	5.0	1.1	0.94
	10	1.0	1.0
0.18	0.1	1.0	0.76
	0.2	0.83	0.70
	0.5	0.71	0.67
	1.0	0.67	0.66
	2.0	0.65	0.66
	5.0	0.59	0.67
	10	0.63	0.68
0.12	0.1	0.76	0.63
	0.2	0.60	0.60
	0.5	0.53	0.59
	1.0	0.50	0.58
	2.0	0.50	0.58
	5.0	0.60	0.59
	10	0.62	0.59

pH	10³[dmg], M	10²k_d, s⁻¹	pH	10³[dmg], M	10²k_d, s⁻¹
11.5	0.1	0.38	10.7	0.1	0.39
	0.2	0.41		0.2	0.41
	0.5	0.41		0.5	0.40
	1.0	0.40		1.0	0.41
11.1	0.1	0.41			
	0.2	0.39			
	0.5	0.41			
	1.0	0.38			

[a] μ = 1.2 M and T = 25 °C; [Ag^{III}]₀ was between 1 × 10⁻⁵ M and 1 × 10⁻⁴ with dmg in large excess.
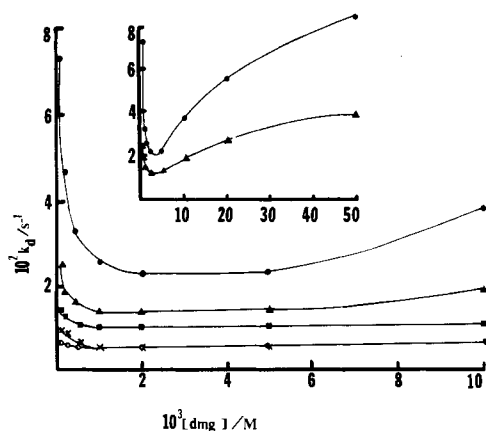
Figure 2. Observed first-order rate constants for Ag(dmg)₂(H)₂⁺ decomposition at 25 °C and 1.2 M ionic strength. [OH⁻]: (●) 1.2 M; (△) 0.72 M; (■) 0.36 M; (X) 0.18 M; (O) 0.12 M.

Scheme II

P = Products include Ag(OH)₂⁻, L, (L)ₒₓ
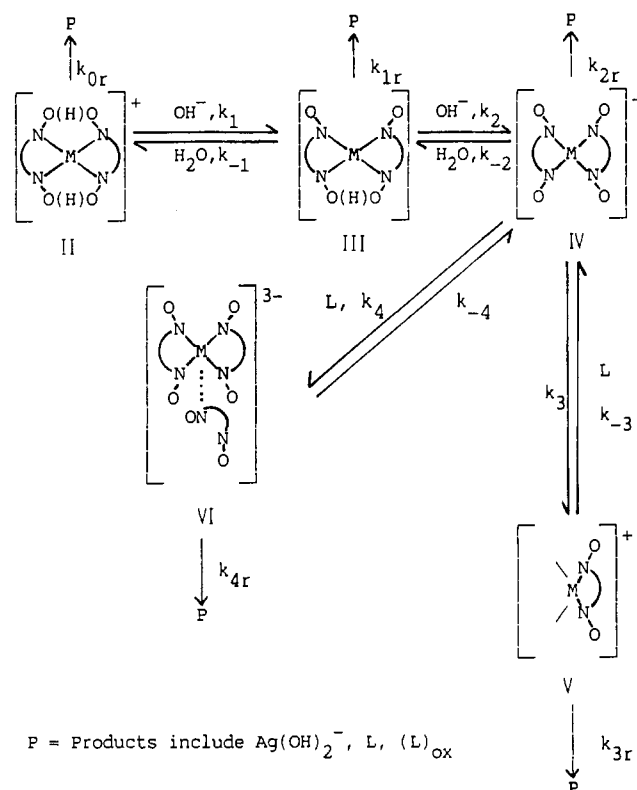
at [dmg] = 0.01 M (seven values of [OH⁻]) gave convincing evidence for zero-, first-, and second-order hydroxide dependences. Experiments in the pH range 10.7–11.5 also gave a value of k_d = (4.0 ± 0.1) × 10⁻³ s⁻¹ independent of both [OH⁻] and [dmg].

Equation 3 represents the simplest function to give a satisfactory fit (r^2 > 0.98) when a nonlinear least-squares analysis was applied to the data of Table IV ([OH⁻] ≥ 0.12 M). The values of the

$$k_d = A + B[OH^-] + D[OH^-]^2/[L] + E[OH^-]^2[L] \quad (3)$$

four parameters, when a $1/k_d$ weighting was used, are A = (4.4 ± 0.3) × 10⁻³ s⁻¹, B = (1.2 ± 0.1) × 10⁻² M⁻¹ s⁻¹, D = (3.4 ± 0.4) × 10⁻⁶ M⁻¹ s⁻¹, and E = 1.0 ± 0.1 M⁻³ s⁻¹. These values were used for k_d(calcd) found in Table IV. There was no significant change in the results when weighting was omitted or when A was held constant at the low hydroxide limit of 0.004 s⁻¹. The inclusion of a ligand-independent, hydroxyl-squared term, $C[OH]^2$, caused only a slight improvement in the fit and had only minor effect on the other four parameters. We estimate the value of C to be less than 4 × 10⁻³ M⁻² s⁻¹.

A reaction scheme proposed to account for the observed kinetic data is presented in Scheme II. Application of the steady-state approximation to species III–VI leads to eq 4, where $k_n/k_{-n} = K_n$ and the pseudoconstants k'_{nr} correspond to the empirical quantities as $k_{0r} = A$, $k'_{1r} = B$, $k'_{2r} = C$, $k'_{3r} = D$, and $k'_{4r} = E$.

$$k_d = k_{0r} + (k_{1r}K_1)[OH^-] + (k_{2r}K_1K_2)[OH^-]^2 +$$
$$(k_{3r}K_1K_2K_3)[OH^-]^2/[L] + (k_{4r}K_1K_2K_4)[OH^-]^2[L]$$
$$= k_{0r} + k'_{1r}[OH^-] + k'_{2r}[OH^-]^2 +$$
$$k'_{3r}[OH^-]^2/[L] + k'_{4r}[OH^-]^2[L] \quad (4)$$

The limiting rate constant at low hydroxyl concentration, k_{0r}, represents the solvent-assisted decomposition of the predominant species, ML₂(H)₂⁺ (II). In almost all known complexes derived from dioximates, the proton-bridged structures impart increased stability by forming a pseudomacrocyclic environment.[19,24,26] The best-known example of this effect is Ni(dmgH)₂,[24] with which Ag(dmgH)₂⁺ is expected to be isostructural. Only copper(II), which forms oxygen-bonded and polynuclear dioximate complexes, is not stabilized in this manner.

The absence of a significant $C[OH^-]^2$ term from eq 3 indicates that there is little or no detectable contribution to the rate from
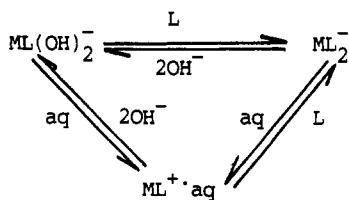
the nonprotonated species, IV. This is probably due more to the formation and redox reactivity of V and VI than to a greatly enhanced redox stability of IV over II. It might be expected, however, that, although species II has an enhanced formation constant, the additional positive charge would serve to destabilize the higher oxidation state of silver.

Application of the steady-state approximation to species III–VI is consistent with the observed pseudo-first-order kinetics. Furthermore, there was no significant spectral change in the visible region when solutions of the complex were rapidly scanned at different [OH⁻]. However, deprotonation is well established in almost all the systems containing H-bridges discussed earlier. Even the stubborn, scarlet-red and practically water-insoluble Ni(dmgH)$_2$ dissolves in strong aqueous alkali, forming a pale yellow solution, because of deprotonation of the bridge hydrogens. The pseudooctahedral Co(dmgH)$_3$ and the Ni(dmg)$_2$(dmgH)$^-$ species are also deprotonated in alkaline solutions. It was found earlier that there is little difference in the spectrum of the deprotonated Ni(dmg)$_3^{2-}$ species from that of the H-bridged Ni(dmg)$_2$-(dmgH)$^-$.[19] Since the deprotonation of the bridged hydrogen involves only a slight change in the periphery of the complex without significantly influencing the bond energies, the intensity of the spectral band should change only slightly without altering the band energies. Therefore, the lack of any tangible spectral change does not rule out the presence of small amounts of the deprotonated species.

Although potentiometric titrations of the complexes were not successful due to the stability constraints, significant deprotonation does, indeed, seem unlikely. At lower [OH⁻] the reactant silver(III) forms a species Ag(OH)$_3$OH$_2$, the pK_a of which has been estimated to be ~11.[13] In view of the higher basicity of the dioximate oxygen,[19] the pK_a(s) for bridge-proton dissociation should be much higher. If the observation that the deprotonation of planar Ni(dmgH)$_2$ occurs at pH > 14 is any indication,[19] then the first pK_a of AgL$_2$(H)$_2^+$ should lie well above 13.

Evidence for the occurrence of five-coordinated species is abundant in d^8 planar systems in general[29] and in Ag(III) systems in particular.[30] The operation of a five-coordinate intermediate, VI, in the present case explains the rate enhancement observed at high [dmg] and high [OH⁻].

The monodioxime species ML$^+$·aq (V) could be produced from IV in the k_3 step (in which it is assumed that a bidentate ligand is released by two aqua groups in two successive steps) or it could come from the ML(OH)$_2^-$ species (cf. Scheme I) by rapid aquation.

In either case the involvement of V is required to explain the observed [OH]^2/[L] dependence.

The lack of any spectral change during decomposition at low [L] rules out a discernibly stable dissociated species prior to electron transfer. The absence of an ESR signal also suggests that neither an Ag(II) nor an Ag(III)–ligand radical ion species is involved. While the steps labeled k_{1r} and k_{2r} may involve redox either before or after ring opening, this is not possible for the path with the inverse [L] dependence. The cleavage of a metal–nitrogen bond in IV is envisaged as the rate-determining step (k_3), which is followed by ligand loss and rapid two-electron transfer to the central Ag(III). A similar situation has been observed in the decomposition reactions of other higher valent metal complexes.[19b,31,32]

There is a fundamental difference in the mechanisms of decomposition of Ni(dmg)$_3^{2-}$[19b] and the present Ag(III)–dmg complex, Ag(dmg)$_2$(H)$_2^+$. The Ni(dmg)$_3^{2-}$ species, like Co(dmg)$_3^{3-}$, is pseudooctahedral (D_3, 3d^6 configuration) and is destablized by (outside) protonation. On the other hand, the AgL$_2$(H)$_2^+$ (with a d^8 configuration and probably with a planar geometry similar to that of dmg complexes of Ni(II), Pd(II), and Pt(II))[24] undergoes base-catalyzed decomposition through the process of deprotonation. Here again one can rationalize that deprotonation prevents the stability due to the pseudomacrocyclic structure, and hence there is ring opening with concomitant electron transfer.

The presence and strength of the H-bridges in all the dioximate complexes of Ag(III) studied can qualitatively account for the relative stability pattern. Compared to unsubstituted glyoximate, the electron-releasing cyclohexyl and methyl groups increase the charge density on the donor nitrogens and the H-bridge-attached oxygens, thereby increasing the formation or decreasing the instability/decomposition or both. The converse is true for the electron-withdrawing phenyl groups and much more markedly for the α-furyl groups (for which no complex formation has been observed).

In this work, we have added trivalent silver to the list of metals that form dioximate complexes. As additional studies of dioximate complexes of higher valent metals become available, a more general explanation of both thermodynamic and kinetic stability can be attempted.

(29) (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; Chapter 5. (b) Catalini, L. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *9*, 269.

(30) (a) Kirschenbaum, L. J. *J. Inorg. Nucl. Chem.* **1976**, *38*, 881. (b) Borish, E. T.; Kirschenbaum, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 749. (c) Kirschenbaum, L. J.; Rush, J. D. *Inorg. Chem.* **1983**, *22*, 3304.

(31) (a) Van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880. (b) Palmer, D. A.; Van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 1009.

(32) (a) Banerjee, R. N.; Banerjea, D. *Indian J. Chem.* **1979**, *17A*, 246. (b) Rybka, J. S.; Kurtz, J. L.; Neubecker, T. A.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 2791. (c) Neubecker, T. A.; Kirksey, S. T., Jr.; Chellappa, K. L.; Margerum, D. W. *Inorg. Chem.* **1979**, *18*, 444.