Organomercury(II) Derivatives of 2-Thiouracil. An Infrared and Proton Magnetic Resonance Study of Structures

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The novel complexes $RHg(s^2UraH_{-1})$ (R = Me, Ph) where s^2UraH_{-1} is the monoanion of 2-thiouracil, have been synthesized. Comparison of the infrared spectra of the solid complexes and of ^1H nuclear magnetic resonance spectra of the complexes in dimethyl-d_6 sulfoxide with spectra of s^2 Ura and $Na[s^2UraH_{-1}]$ allows the recognition of the existence of isomers in the solid, with bonding to exocyclic sulfur and to pyrimidine nitrogens. In solution, a simpler pattern is observed, with $^2J(^1H-^{199}Hg)$ indicating bonding to sulfur only.

Introduction

The aim of this work is twofold: to obtain information on the binding of a heavy metal ion to a minor pyrimidine constituent of the nucleic acids, since there is a continuing interest in mutagenic and cytotoxic effects of heavy metals arising by interactions with nuclear DNA [1]. Secondly, since derivatives of 2-thiouracils are the drugs of choice in the treatment of hyperthyroidism, and elevated metal ion (copper) levels are observed in conjunction with these conditions [2], we deemed it interesting to point out which are the likely coordination sites of the metals. The methylmercury(II) cation which binds much as other heavy metals do to a variety of ligand sites ranging from P, S, N, O and C atoms [3] serves as a good probe ion because it is unifunctional, gives complexes with a well defined stereochemistry and readily participates in electrophilic substitution. While the early studies [4] generally assumed that the isomers of the mercuriated forms were analogous to those of the protonated forms, it was later pointed out by Tobias [5] that many metals interact at different sites from the proton.

The lactam-thione structure of 2-thiouracil is confirmed by X-ray [6] and apparently the same tautomeric form is preserved in acidic and neutral aqueous solution [7]; with further increase in pH two equilibria have been demonstrated spectrophotometrically, considered first to give the mono anion with the negative charge delocalized between oxygen and sulfur, and next the dianion with negative charges localized on sulfur and oxygen. As for the metal complexes, copper(I) is shown by X-ray structure determination to bind to sulfur atoms in bis(2-thiouracil)-chlorocopper(I) dimethylformamide solvate [2], the ligand being in the lactam-thione form.

The interesting mercurial tetrakis(acetoxymercuri)methane [8] is reported to bind selectively to the sulfur atom of 6-thioguanosine and to the 4-thiouridine residue of *E. coli* $tRNA^{val}$. In the presence of the Mg^{2+} ion little, if any, binding of methylmercury(II) chloride was observed [9]. However, under the same conditions, both $HgBr_2$ did bind to the 4-thiouridine residue. Removing Mg^{2+} and heating to 40 °C enabled CH_3Hg^+ to bind to the thiolated base. Pentafluorophenylmercury(II) chloride is also reported [10] to bind to s^4U in $tRNA^{tyr}$ to give a derivative with a covalent Hg–S bond. The synthesis and characterization of 2-thiouracil complexes provides evidence that sulfur cannot be assumed to be the only site of metallation and that the presence of various isomers cannot be discounted.

Experimental

2-thiouracil (EGA) and phenylmercuric nitrate (FLUKA) are commercially available and were purified by recrystallization from suitable solvents. Methylmercuric nitrate was prepared by reaction of

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the chloride (in slight excess) with silver nitrate in a water/ethanol mixture. The suspension was stirred for two days and filtered. The filtrate was slowly evaporated to give crystalline methylmercuric nitrate. The sodium salt of 2-thiouracil was prepared by reacting the ligand with an equivalent amount of sodium methoxide in dry methanol [11] and evaporating to dryness.

Preparation of the Complexes

MeHg(s^2 UraH$_{-1}$)

Methylmercuric nitrate (1.083 g, 3.90 mmol) was added to a solution of Na(s^2UraH$_{-1}$) obtained by reacting the ligand (0.500 g, 3.90 mmol) with an equivalent amount of sodium methoxide in dry methanol (30 ml). After the solution was stirred for 4 hours and filtered to remove some off-white solid, it was kept at −20 °C for two days. The white solid was collected, washed with dry methanol and dried over P_4O_{10} at atmospheric pressure. A further crop of the solid compound was recovered from the solution left standing at −20 °C. Total yield: 1.025 g, 75%. Analytical data (%), calculated for $C_5H_6N_2$ OSHg: C, 17.52; H, 1.76. N, 8.17. Found: C, 17.80; H, 1.70; N, 8.02. M.P. (unc.) 190 °C (decomp.).

Caution: use a well ventilated fume-hood for all operations. Accidental skin contact with the solid causes small painful ulcers.

PhHg(s^2 UraH$_{-1}$)

Phenylmercuric nitrate (1.280 g, 3.16 mmol) was dissolved in warm dry methanol (60 ml) and added to a methanolic solution (20 ml) of the sodium salt of the ligand (0.410 g, 3.20 mmol). After stirring the clear solution (a small opalescence appears at the beginning) by heating gently for 2 hours, it was kept at −20 °C overnight. A white precipitate appeared, which was collected, washed with dry methanol and dried under vacuum over P_4O_{10}. Yield: 0.850 g, 66%.

Analytical data (%), calculated for $C_{10}H_8N_2$-OSHg: C, 29.67; H, 1.99; N, 6.92; S, 7.92. Found: C, 29.40; H, 1.90; N, 6.47; S, 7.07. M.P. (unc.) 165 °C.

Microanalyses were performed by Laboratorio di Microanalisi, Istituto di Chimica Organica dell' Università, Milano, Italy, and by Microanalytical Laboratory, TNO, Utrecht, The Netherlands. The infrared spectra (4000–180 cm^{-1}) were measured with a Perkin-Elmer Model 580 spectrophotometer as split mulls using CsI windows. Spectra in DMSO solution were obtained using both variable pathlength and 0.5 mm pathlength KBr cells using a compensation technique (see W. J. Potts, Jr., 'Chemical Infrared Spectroscopy', Vol. 1, Techniques, Wiley, New York, 1963). ^{1}H N.M.R. spectra were measured with Varian EM 360 A (operating at 60 MHz) and FT 80 A (operating at 80 MHz in the FT mode) instruments. Temperature of the probe was *ca.* 31 °C. DMSO-d_6 was dried over molecular sieves (3A type).

Results and Discussion

Extensive work has been done by Tobias and coworkers [12] on the binding of methylmercury(II) to pyrimidine bases, nucleosides and nucleotides. CH_3Hg^+ binding to uridine and cytidine at N(3) was assessed by Raman difference spectroscopy. Lord and Thomas [13] investigated the interaction of $HgCl_2$ with the same moieites, using Raman spectroscopy, and N(3) was assigned as the binding site. In an approach to the synthesis of 2-thiopyrimidine nucleosides, by use of the condensation of the mercury(II) salts with glycosyl halides, a chloromercury-(II) salt of 2-thiouracil has also been reported [14, 15]. In this context [14], the synthesis of a S(2)-ribofuranosyl-2-thiouracil was first reported. It was necessary to add mercury(II) bromide to the reaction mixture in order to effect N-glycosylation and the N(3)- and N(1)-glycosyl derivatives were obtained in the ratio of 3:1. Under appropriate conditions, both the chloromercury(II) and bromomercury(II) salts of 2-thiouracil gave N(1)-glycosides exclusively. In addition, reactions of the chloromercury(II), silver(I) and thallium(I) salts of 2-thiouracil with acetobromoglucose afforded a S(2)-monoglucoside and a S(2), O(4)-diglucoside. Tentatively, the binding of metal ions to 2-thiouracil might be inferred by the nature of the substitution products obtained. The reaction of a heavy metal salt of 2-thiouracil with a glycosyl halide appears to depend on three factors: (a) the structure of the metal salt (*i.e.* the relative donor properties of N(1), S(2), N(3) and O(4) atoms of the deprotonated base), b) the ease with which S(2)- and O(4)-glycoside groups are cleaved or rearranged, and c) the steric effect of the exocyclic oxygen and sulfur atoms.

Infrared Spectra

Assignment of structures for the complexes by comparison of I.R. spectra changes following the metallation requires caution, since the corresponding monoanions of 2-thiouracil, for which an extensive charge delocalization has been proposed, might consist of an equilibrium mixture of two tautomers, as reported for the 4-thiouracil monoanion [16].

2-Thiouracil Vibrations

Three features in the IR spectra which enable one to differentiate between the mercapto and thione forms of the complexes are the presence, absence or shifts of strong absorption:

TABLE I. Relevant Infrared Absorptions.[a]

Compound	ν(NH)	ν(C=O)[b]	ν(C=S)[b]	ν(Hg–C)	ν(Hg–S)
			1560s,bd		
s^2Ura	3190m	1702s	1172m		
	3130m	1682s	1155m		
Na[s^2UraH$_{-1}$]	3140m,bd	1610m,sh			
		1575s,bd			
MeHg(s^2UraH$_{-1}$)	3050s	1665s (1680s,bd)	1522s	565mw (550s)	
		1652s (1650s)	1170m	560mw	220m
			1160m	542mw	
PhHg(s^2UraH$_{-1}$)	3120s	1665w	1540s		245m
		1593s	1172m		

[a]Abbreviations: s = strong, m = medium, w = weak, bd = broad, sh = shoulder. Values given in parenthesis refer to solutions in DMSO. [b]The band assignments are discussed in the text.

i) in the range 1720–1640 cm^{-1}, due to ν(C=O) stretching vibrations and to skeletal stretching modes.

ii) vibrational modes where thiocarbonyl stretching contributes (thioamide band I and II).

iii) ν(N–H) stretching band.

Relevant I.R. data are reported in Table I.

In the range 3300–2800 cm^{-1} vibrations due to ν(N–H) and ν(C–H) are expected. A band at 3145 cm^{-1} (3130 cm^{-1} this work) has been tentatively assigned [17] to ν(N–H) vibrations of s^2Ura, which is lacking both in Na[s^2UraH$_{-1}$] and K[s^2UraH$_{-1}$] [18], and appears to be shifted at 3120 cm^{-1} in PhHg(s^2UraH$_{-1}$); a weak absorption at 3150 cm^{-1} is present in MeHg(s^2UraH$_{-1}$). In the free ligand absorptions are present at 3080 and 3045 cm^{-1}, the latter is either absent or much reduced in intensity in the complexes. Solid 2-thiouracil has been reported [18] to have I.R. absorptions at 1705 and 1681 cm^{-1}. The nature of these modes is not exactly known, but in related uracil [19] and uridine [20] absorptions in this region have been assigned as ν(C=O) for the higher frequency band and in phase ν(C$_4$=O) + ν(C$_5$=C$_6$) for the lower frequency band. These vibrations are lowered to 1665 and 1652 cm^{-1} on formation of MeHg(s^2UraH$_{-1}$). Only minor changes are observed in going from the solid to a DMSO solution, the broad band at 1680 cm^{-1} being probably due to only partial compensation of the solvent. In the solid Na[s^2UraH$_{-1}$] a broad band is observed at 1575 cm^{-1} along with a medium one at 1610 cm^{-1}. Since a marked shift to lower frequency of ν(C=O) is observed both with anions of purines and pyrimidines [1, 16] and complexes, it can be attributed to deprotonation of the base and not necessarily to metal–oxygen interactions.

In the solid Na[GuoH$_{-1}$]·H$_2$O the ν(C=O) absorption is shifted to 1595 cm^{-1} from 1730 cm^{-1} in the neutral ligand, while in the MeHg(GuoH$_{-1}$) complex this band is located at 1625 cm^{-1}. This is consistent with increased electron delocalization in the base resulting in a decreased bond order for the carbonyl group. In the complexes with guanosine it is deprotonation of N(1) which leads to coordination of MeHg^{II} in MeHg(GuoH$_{-1}$), but a similar shift of ν(C=O) frequency has also been observed [16] with the monoanion of 4-thiouracil which exists in solution as an equilibrium mixture of two monoanionic tautomeric forms equivalent to II and III each arising from deprotonation at N(3) and N(1) respectively. As to the existence of tautomers in the solid, a comparison with the spectrum of PhHg(s^2UraH$_{-1}$) suggests that in the latter at least two of these are present. In fact, the 1665 cm^{-1} absorption is present in both, although with much reduced intensity in the PhHg^{II} derivative, while the 1615 and 1593 cm^{-1} bands resemble closely those of Na[s^2UraH$_{-1}$]. Moreover, the 1632 cm^{-1} absorption (sh) can be reasonably assigned to a pyrimidine ring vibration and it appears to be not very sensitive to metallation, while the band at 1560 cm^{-1} (thioamide band I) [21] does show some marked change (1522 cm^{-1} in MeHg (s^2UraH$_{-1}$), 1540 cm^{-1} in PhHg(s^2UraH$_{-1}$)). On the contrary, the absorptions assigned [21] as thioamide band II + amide band III are less sensitive to complexation (see Table I).

Features associated with CH_3Hg^{II}

The (Hg–C) stretching frequency is moderately sensitive to the ligand *trans* to the methyl group [12] varying from 566 cm^{-1} with H$_2$O to 525 cm^{-1} with I$^-$, hence it has previously been used to distinguish between O- and S-coordination [22] and between C- and O-coordination as well [3]. For oxygen donors the ν(Hg–C) vibration occurs between 580 and 565 cm^{-1}, while for C-atom donors it lies between 565 and 545 cm^{-1}. Sulfur bonded derivatives have in general a somewhat lower value of ν(Hg–C), as in MeHg(S$_2$CNEt$_2$) (528 cm^{-1}) [23] and in the L-cysteinato complex (538 cm^{-1}) [24].

TABLE II. ^{1}H N.M.R. Data for 2-Thiouracil Complexes.[a,c]

Species Compound[b]	H_5	H_6	H(N)	RHg^{II}	$^2J(^1H-^{199}Hg)$
2-thiouracil (s^2Ura)	5.91d[d]	7.48d[d]	12.13bd		
$CH_3Hg(s^2UraH_{-1})$	5.95d[e]	7.57d[e]	11.99bd	0.74 [h]	191.8[i]
$C_6H_5Hg(s^2UraH_{-1})$	6.06d[f]	7.70d[f]			
$Na[s^2UraH_{-1}]$	5.46d[g]	7.35d[g]			

[a]In dimethyl-d_6 sulfoxide; chemical shifts δ (ppm) from internal tetramethylsilane. [b]The IUPAC–IUB abbreviations are employed; see *Biochemistry, 9,* 4022 (1970). Since s^2Ura is the normal abbreviation for 2-thiouracil, we have used s^2UraH_{-1} for the conjugate base, see Ref. 5(b). [c]d = doublet; bd = broad. [d]The spectrum is in good agreement with that reported in Ref. 17. J_{H_5,H_6} = 7.5 Hz. [e]$J_{H_5-H_6}$ = 6.8 Hz. [f]$J_{H_5-H_6}$ = 7 Hz. [g]$J_{H_5-H_6}$ = 6 Hz. [h]A resonance at δ 7.44 ppm is broad and integrates for 5 protons. A doublet of signals (less than 1 proton) is present at 9 ppm. It cannot be assigned to a NH proton, since it remains unchanged after addition of a few drops of D_2O to the solution. [i]Coupling constant (Hz) due to the methyl protons; the sign of the coupling constant is assumed to be negative (see H. F. Henneike, *J. Am. Chem. Soc., 94,* 5945 (1972)).

For $MeHg(s^2UraH_{-1})$ the observed values of ν(Hg–C) (565, 560 and 542 cm^{-1}) are intriguing in the sense that they clearly indicate the occurrence of methylmercury(II) moieties bonded to different sites but cannot unambiguously be assigned to a specific one. Moreover, in this region, free ligand vibrations occur at 548 and 522 cm^{-1} and essentially on the basis of their higher intensities they are assigned to a doublet of absorptions at 520 and 505 cm^{-1}. In DMSO solutions the free ligand shows two absorptions at 530 and 495 cm^{-1} while the $MeHg(s^2UraH_{-1})$ complex has absorptions at 550, 520 and 505 cm^{-1}; only the higher frequency vibration might be associated with the organometallic moiety and a simpler pattern (possibly indicating only one species) is observed in respect to the spectrum of the solid.

ν(Hg–S) stretching vibrations in thiolato complexes are observed in the region 350–300 cm^{-1} [25]; at lower frequencies, vibrations assigned to ν(Hg–s) are reported for adducts of mercury(II) halides with N,N′-substituted thioureas [26] and multidentate heterocyclic compounds such as thiazolidine thiones [27]. Both $MeHg(s^2UraH_{-1})$ and $PhHg(s^2UraH_{-1})$ exhibit medium intensity bands at 220 and 245 cm^{-1} respectively, in a region free from ligand vibrations, which may tentatively be assigned to ν(Hg–S).

^{1}H NMR Spectra and Structures of the Complexes

Not only do the ^{1}H NMR spectra yield information relating to the ligand but also effects of the complexation on the (organo) metal ion can be monitored via the chemical shift of the methyl protons and the two-bond coupling constant between the ^{199}Hg isotope and the methyl protons, $^2J(^1H-^{199}Hg)$.

The latter parameter is inherently more sensitive to the strength of metal ligand bond, as is reflected in correlations between the coupling constant and the logarithm of the stability constant of the metal-ligand complexes [28]. The ^{1}H NMR data for the $RHg(s^2UraH_{-1})$ complexes in DMSO-d_6 are reported in Table II. In the $MeHg(s^2UraH_{-1})$ complex the presence of a broad ligand proton resonance at δ 11.99 ppm due to a N–H proton is in agreement with isomers IV–VII reported in Fig. 1. The value of the coupling constant however (^2J = 191.8 Hz) strongly suggests the presence of isomer VI, since it fits well in the rationalization proposed by Rabenstein [28]. On the other hand the ionic formulation (VII) may be excluded on the basis of the value of the coupling constant [29] for the DMSO–CH_3Hg^+ complex (^2J = 260.6 Mz). Moreover, both $HgCl_2$

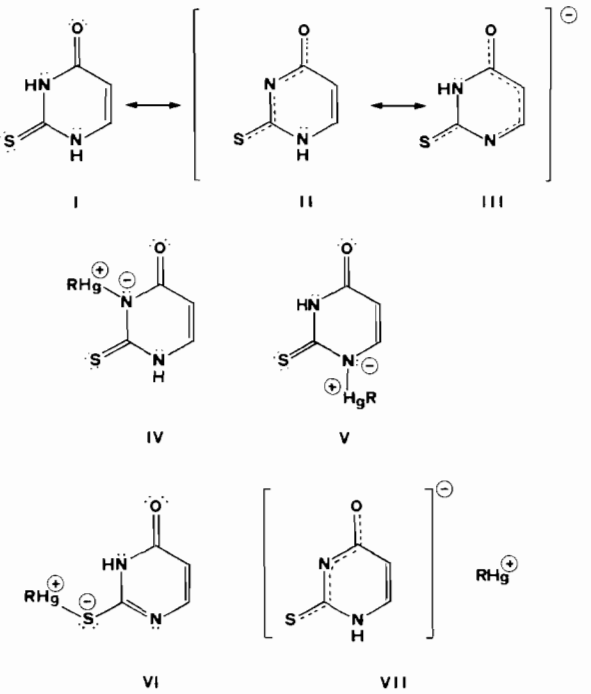

Fig. 1. Structures of isomers IV–VII.

and CH_3HgCl are reported [31] to bind essentially to the sulfur atoms of s^6Guo and s^8Guo in a ^1H and ^{13}C NMR study of the (organo)mercury(II) interaction with thiolated nucleosides in DMSO. $^2J(^1H-^{199}Hg)$ values are not reported in this context.

The signal at *ca.* δ 12 ppm is lost in the spectrum of PhHg(s^2UraH$_{-1}$). This result suggests either a rapid exchange of the proton at N(3) upon binding to the sulfur atom (VI), as proposed [30] for the case of the complexes with s^8Guo and for the MeHg(s^2UraH$_{-1}$) complex, or bonding to a deprotonated N of the pyrimidine base (IV + V) and to exocyclic sulfur. In the latter case the ligand may act as anionic bidentate, and a fast exchange between the two tautomeric forms IV and V is likely to occur, since no NH signal is detected in the spectrum of Na[s^2UraH$_{-1}$] where such equilibrium is known to exist. Further evidence for these structures comes from trends in H_5 and H_6 protons. Both MeHg and PhHg complexes exhibit downfield shifts of the C(5) and C(6) protons, the largest chemical shift changes occurring for the PhHg(s^2UraH$_{-1}$) complexes (Table II). A similar downfield shift was observed for the methylmercury(II) complex with 2-mercapto pyrimidine [31], whose X-ray structure is also reported, and bonding to sulfur is again observed, along with a weak coordination to nitrogen.

Concluding Remarks

The solid complexes RHg(s^2UraH$_{-1}$) (R = Me, Ph) are shown by I.R. spectroscopy to be a mixture of isomers, according to the presence of multiple (Hg–C) vibrations in MeHg(s^2UraH$_{-1}$) which may be associated with organometallic moieties bonded to different donor atoms (exocyclic S(2), N(3), N(1) being the likely binding sites). The same holds true for the $PhHg^{II}$ derivative, where the ν(C=O) vibration is more conveniently taken as diagnostic band. The possible structures which are suggested are in agreement with the nature of the products of glycosylation [14, 15]. In DMSO-d_6 solution, the presence of a single signal due to the organometallic moiety and the value of $^2J(^1H-^{199}Hg)$ coupling constant agrees with the presence of only one chemical species in solution, with methylmercury(II) cation bonded to the thiolato group while the disappearance of the N–H signal in both PhHg(s^2(UraH$_{-1}$) and Na[s^2-UraH$_{-1}$] suggests the occurrence of an equilibrium between isomers.

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References

1 A. J. Canty and R. S. Tobias, *Inorg. Chem., 18,* 413 (1979) and ref. therein.
2 a) G. W. Hunt and E. L. Amma, *J. Chem. Soc. Chem. Comm.,* 869 (1973).
b) G. W. Hunt, E. A. H. Griffith and E. L. Amma, *Inorg. Chem., 15,* 2993 (1976).
3 J. M. T. Raycheba and G. Geier, *Inorg. Chem., 18,* 2486 (1979).
4 R. B. Simpson, *J. Am. Chem. Soc., 86,* 2059 (1964).
5 a) S. Mansy and R. S. Tobias, *J. Am. Chem. Soc., 96,* 6874 (1974).
b) G. Y. H. Chu, R. E. Duncan and R. S. Tobias, *Inorg. Chem., 16,* 2625 (1977) as a reference to pyrimidine nucleosides related to this work.
6 D. Tsernoglou, *Ph.D. Thesis,* Yale Univ., New Haven, 1966, quoted by J. S. Kwiatkowski and B. Pullman, *Advan. Heterocycl. Chem., 18,* 199 (1975).
7 D. Shugar and J. J. Fox, *Bull. Soc. Chim. Belg., 61,* 293 (1952).
8 a) J. J. Lipka, H. Bazari, C. Levinthal and S. J. Lippard, *Biophys. J., 25,* 42a (1970).
b) K. G. Strothkamp, J. Lehmann and S. J. Lippard, *Proc. Natl. Acad. Sci. U.S.A., 75,* 1181 (1978).
9 H. R. Sunshine and S. J. Lippard, *Nucleic Acids Res., 1,* 673 (1974).
10 A. S. Jones, R. T. Walker and V. Youngs, *Biochim. Biophys. Acta, 299,* 293 (1973).
11 J. Peeling, F. E. Hruska, D. M. McKinnon, M. S. Chauhan and N. S. McIntyre, *Can. J. Chem., 56,* 2405 (1978).
12 S. Mansy, T. E. Wood, J. C. Sprowles and R. S. Tobias, *J. Am. Chem. Soc., 96,* 1762 (1974).
13 R. C. Lord and G. J. Thomas, Jr., *Biochem. Biophys. Acta, 142,* 1 (1967).
14 H. J. Lee and P. W. Wingler, *Biochemistry, 7,* 1427 (1968).
15 G. T. Rogers and T. L. V. Ulbricht, *J. Chem. Soc., (C),* 2995 (1971).
16 A. Psoda, Z. Kazimirczuck and D. Shugar, *J. Am. Chem. Soc., 96,* 6832 (1974).
17 F. Parmentier, H. Beernhaert and S. Van Vlasselaer, *Farm. Tijdschr. Belg., 52,* 460 (1975).
18 W. Beck and N. Kottmair, *Chem. Ber., 109,* 970 (1976).
19 H. Susi and J. S. Ard, *Spectrochim. Acta, Part A, 27a,* 1549 (1971).
20 R. C. Lord and G. J. Thomas, Jr., *Spectrochim. Acta, Part A, 23a,* 2551 (1967).
21 I. P. Khullar and U. Agarwala, *Aust. J. Chem., 28,* 1529 (1975).
22 D. L. Rabenstein, M. C. Tourgangeau and C. A. Evans, *Can. J. Chem., 54,* 2517 (1976).
23 C. Chieh and L. P. Leung, *Can. J. Chem., 54,* 3077 (1976).
24 N. J. Taylor, Y. S. Wong, P. C. Chieh and A. J. Carty, *J. Chem. Soc., Dalton Trans.,* 438 (1975).
25 G. C. Stocco, *Inorg. Chim. Acta, 24,* L65 (1977).
26 G. Marcotrigiano, G. Peyronel and R. Battistuzzi, *J. Inorg. Nucl. Chem., 37,* 1675 (1975).
27 M. R. Udupa and M. Padmanabhan, *Inorg. Chim. Acta, 13,* 239 (1975).
28 D. L. Rabenstein, *Acc. Chem. Res., 11,* 100 (1978).
29 A. J. Brown, O. W. Howarth and P. Moore, *J. Chem. Soc., Dalton Trans.,* 1589 (1976).
30 K. W. Jennette, S. J. Lippard and D. A. Ueko, *Biochim. Biophys. Acta, 402,* 403 (1975).
31 C. Chieh, *Can. J. Chem., 56,* 560 (1978).