of these observations, a consistent structural model for this compound has been proposed.

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Multidentate Ligand Kinetics. XIII. Lead(II) and Copper(II) Suppression of Their Rate of Exchange with 1,2-Diaminocyclohexanetetraacetatocadmate(II)

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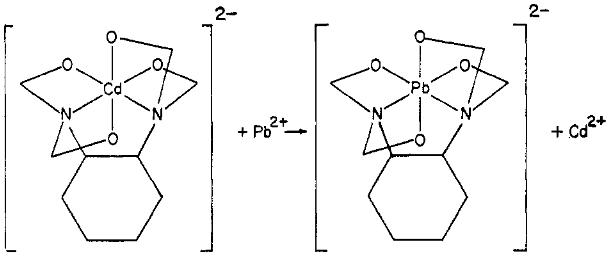
The rate of Pb(II) substitution of Cd(II) in $CdCyDTA^{2-}$ (CyDTA is *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate) decreases as the concentration of Pb(II) increases. This is an example of an exchange reaction in which a reactant suppresses its own rate of exchange. The anomaly results from the steric requirements of CyDTA which prevent the direct exchange of metal ions. Instead the exchange rate is controlled by a hydrogen ion reaction with $CdCyDTA^{2-}$. Lead(II) forms weak complexes with the acetate groups of $CdCyDTA^{2-}$ and these complexes block the hydrogen ion reaction. Hence excess Pb^{2+} slows the rate of appearance of $PbCyDTA^{2-}$. Copper behaves in a similar manner.

Introduction

As in the exchange reactions of other metal–CyDTA complexes,[2,3] there is no direct metal ion attack on the cadmium–CyDTA complex and the rate of the reaction in eq 1 does not increase with the lead ion concentration. Sterically it is not possible to bind both cadmium and lead to the two nitrogen atoms of CyDTA. As a result the most important kinetic path is hydrogen ion displacement of cadmium followed by reaction with lead. However, unlike the previously studied metal–CyDTA exchange systems the rate of formation of product is suppressed by excess concentrations of the exchanging metal ion. Thus the rate of appearance of $Pb(CyDTA)^{2-}$ in eq 1 is decreased by increasing concentrations of lead. The cadmium–CyDTA reaction with copper also becomes slower as the copper concentration increases. In both cases a first-order dependence in hydrogen ion concentration is observed as in all other metal–CyDTA exchange reactions.[2] Suppression of the reaction rate by an excess of the scavenger ion (Pb^{2+} or Cu^{2+}) is attributed to the formation of weak complexes between the scavenger ion and the cadmium–CyDTA complex. Species such as $CdCyDTA^{2-}$–Pb^{2+} are not readily attacked by hydrogen ion. A similar mechanism (eq 2) is proposed when copper ion is the scavenger. As a result, the higher the concentrations of the exchanging metal ion (Pb^{2+} or Cu^{2+}), the slower is the exchange reaction.



(1)

$$\begin{tikzcd}
\mathrm{CdCyDTA^{2-}} \arrow[d, shift right, "\mathrm{Pb^{2+}}"'] & + \mathrm{H^+} \arrow[r, shift left, "k_{\mathrm{H}}{}^{\mathrm{CdCy}}(\mathrm{rds})"] & \mathrm{HCyDTA^{3-}} + \mathrm{Cd^{2+}} \arrow[l, shift left] \arrow[d, "+\mathrm{Pb}^{+}"', "-\mathrm{H}^{+}"', "\mathrm{rapid}"] & (2) \\
\mathrm{Cd(CyDTA)Pb} \arrow[u, shift right] \arrow[d, shift right, "\mathrm{Pb^{2+}}"'] & \left.\begin{array}{l} \text{no} \\ \text{reaction} \\ \text{with} \\ \mathrm{H^+} \end{array}\right\} & \mathrm{PbCyDTA^{2-}} & \\
\mathrm{Cd(CyDTA)Pb_2{}^{2\bullet}} \arrow[u, shift right] & & &
\end{tikzcd}$$

Experimental Section

Solutions of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ were standardized by complexometric titrations with CyDTA or EDTA. The acid form of CyDTA (LaMont Laboratories) was dissolved in NaOH and standardized with copper using Chrome Azurol S indicator. Cadmium–CyDTA solutions were prepared with about 10% excess CyDTA. The ionic strength was controlled at 0.10 M using KNO_3. All reactions were at 25.0 ± 0.1°.

The reactions between $CdCyDTA^{2-}$ and Pb^{2+} were followed by measuring the absorbance of $PbCyDTA^{2-}$ at 260 mμ with a Cary 16 spectrophotometer. The molar absorptivities ($cm^{-1} M^{-1}$) of the species in solution were 1860 for $PbCyDTA^{2-}$, 20 for $CdCyDTA^{2-}$, 3.0 for $Pb(C_2H_3O_2)_n{}^{2-n}$, 1.5 for NO_3^-, and 1.0 for $C_2H_3O_2^-$. The reactions with copper were followed at 310 mμ ($\epsilon_{\mathrm{CuCyDTA}}$ 1099) and 700 mμ ($\epsilon_{\mathrm{CuCyDTA}}$ 111). Most reactions were measured to constant absorbance (A_∞) or for more than 2 half-lives. Excellent first-order plots were observed from log ($A_\infty - A$) against time in accord with the rate expression

$$\frac{d[\mathrm{PbCyDTA^{2-}}]}{dt} = -\frac{d[\mathrm{CdCyDTA}]}{dt} = k_0[\mathrm{Cd(CyDTA)_T}] \qquad (3)$$

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[1] Correspondence to be addressed to this author.

[2] D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, **6**, 283 (1967).

[3] D. W. Margerum and T. J. Bydalek, *ibid.*, **2**, 683 (1963).

where

$$[\mathrm{Cd(CyDTA)_T}] = [\mathrm{Cd(CyDTA)^{2-}}] + [\mathrm{Cd(CyDTA)H^-}] + [\mathrm{Cd(CyDTA)Pb}] + [\mathrm{Cd(CyDTA)Pb_2^{2+}}] \quad (4)$$

and the latter four species are in rapid equilibrium. A similar expression holds substituting copper for lead, except at the copper concentration used only [Cd(CyDTA)Cu] was observed. Conditions were adjusted to make the reverse of the reaction in eq 1 negligible.

Reactions were run without buffer (no pH change during the reaction). The rate was faster in the presence of acetate–acetic acid buffer and this effect also was studied.

Results and Discussion

The exchange reactions all showed a first-order dependence on [Cd(CyDTA)$_T$] in the individual rate plots. The observed rate constants are given in Table I. The reaction also has a first-order hydrogen ion dependence at constant Pb(II) concentrations. When the data are corrected for the small amount of Cd(CyDTA)H$^-$ present at higher acidity (log K_{CdCyH} = 3.0),[4] the k_0 against [H$^+$] plot has a zero intercept. Hence there is no appreciable reaction except by acid attack and various k_0/[H$^+$] values can be compared in studying the effect of Pb(II) and Cu(II) on the reaction.

TABLE I

OBSERVED FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF Cd(CyDTA)$_T$ WITH Pb(II) AND Cu(II)

$10^3[\mathrm{M}^{2+}]$, M	$10^5[\mathrm{H}^+]$, M	$10^5[\mathrm{Cd(CyDTA)_T}]$, M	10^3k_0, sec^{-1}
	M = Pb		
0.60	7.76	8.57	2.92
0.60	8.32	8.57	2.95
1.80	7.24	8.57	2.31
1.80	8.12	8.57	2.46
3.00	1.90	12.8	0.546
3.00	1.95	12.8	0.568
3.00	7.41	12.8	2.20
3.00	7.41	12.8	2.15
3.00	13.2	12.8	3.81
3.00	13.2	12.8	3.67
3.00	19.0	12.8	5.09
3.00	19.5	12.8	5.18
6.00	7.24	12.8	1.29
6.00	7.41	12.8	1.41
10.0	7.58	12.8	0.955
10.0	7.93	12.8	1.03
20.0	16.6	12.8	1.15
20.0	17.8	12.8	1.09
	M = Cu		
0.90	3.80	16.1	1.45
0.90	4.07	16.1	1.42
1.50	4.47	16.1	1.59
1.50	4.57	16.1	1.57
2.20	5.02	16.1	1.69
8.10	12.0	8.57	3.38
15.0	1.15	30.0	0.251
15.0	10.2	30.0	2.04
15.0	12.0	30.0	2.38
20.0	1.66	30.0	0.290
20.0	2.40	30.0	0.413
20.0	10.0	30.0	1.67
20.0	14.8	30.0	2.36

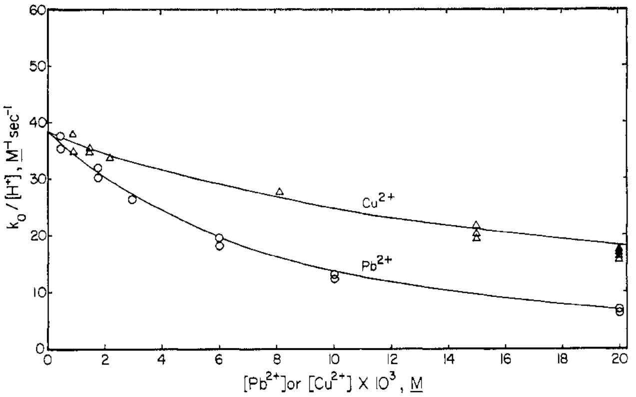
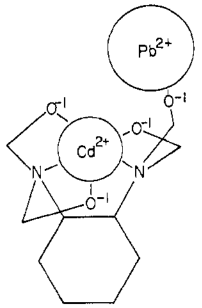


Figure 1.—Lead(II) and copper(II) suppression of the hydrogen ion rate constant with Cd(CyDTA)$_T$. [KNO$_3$] = 0.10 M, 25.0°, no buffer. The curve for lead(II) suppression corresponds to eq 7 using the constants in Table II and assuming pH 4.0. Similarly the curve for copper(II) suppression corresponds to eq 6 assuming pH 4.4. The points are the experimental data.

Figure 1 shows the decrease of the exchange rate constant as the Pb(II) or Cu(II) concentration is increased. This type of suppression of the exchange rate by the exchanging metal ion is unusual and has not been observed in other exchange reactions, and, in particular, it was not found in previous metal–CyDTA systems. However, weak complexes have been observed between Cu(II) and NiEDTA^{2-} where the copper appeared to be coordinated to one of the acetate groups in the nickel complex.[5] A similar type of complex (I) is proposed to account for the kinetic behavior in this case. There are several important differences, however, one being the fact that EDTA complexes have the ability to unwrap and transfer from one metal ion to another whereas the ring prevents this in CyDTA. Therefore Ni(EDTA)Cu is a reaction intermediate while Cd(CyDTA)Pb and Cd(CyDTA)Cu are kinetic dead ends insofar as the transfer reaction is concerned. The latter complexes not only fail to furnish a path for the metal replacement of the Cd(II) inside the coordination cage of CyDTA but they also block the usual hydrogen ion attack. More than 30 other metal–CyDTA systems examined kinetically all have H$^+$ attack as the predominant exchange path and none shows direct metal ion attack leading to exchange.



I

The Ni(EDTA)Cu complex (K = 6.8 in 1.25 M NaClO$_4$) was observed only above 10^{-2} M Cu^{2+} concentrations while the Cd(CyDTA)Cu and Cd(Cy-

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

(5) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).

DTA)Pb complexes have noticeable kinetic effects above 10^{-3} M. This is in part due to the fact that the ionic strength is only 0.10 M in the present study. However, there are several other reasons why the association with $CdCyDTA^{2-}$ may be stronger than that with $NiEDTA^{2-}$. Cadmium is more polarizable than nickel and can more easily accommodate another positively charged ion in the vicinity and cadmium may use fewer coordinating groups than nickel. Lead forms stronger acetate complexes (log $K_1 = 2.1$ compared to 1.8 for copper) and the Cd(CyDTA)Pb complex appears to be about twice as strong as the Cd(CyDTA)Cu complex.

The mechanism in eq 2 gives the rate expression in eq 5 which also takes into account the formation of

$$k_0([CdCyDTA^{2-}] + [Cd(CyDTA)H^-] + [Cd(CyDTA)Pb] + [Cd(CyDTA)Pb_2^{2+}]) = k_H^{CdCy}[H^+][CdCyDTA^{2-}] \quad (5)$$

some of the protonated complex, $Cd(CyDTA)H^-$. The $Cd(CyDTA)Pb_2^{2+}$ complex can be neglected at lower lead concentrations and the data fit the graph of eq 6

$$\frac{[H^+]}{k_0[Pb^{2+}]} = \frac{1}{k_H^{CdCy}}\left(\frac{1 + K_{CdCyH}[H^+]}{[Pb^{2+}]}\right) + \frac{K_{CdCyPb}}{k_H^{CdCy}} \quad (6)$$

which gives $k_H^{CdCy} = 42.4$ and $K_{CdCyPb} = 136$ from the slope and intercept, where K_{CdCyPb} is the stability constant for the complex formation between Pb^{2+} and $CdCyDTA^{2-}$.

Figure 2 is a similar plot of all the terms in eq 5 using $\beta_{CdCyPb_2} = [CdCyPb_2^{2+}]/[CdCy^{2-}][Pb^{2+}]^2$ and the value of 136 for K_{CdCyPb}. The relationship plotted is given in eq 7. Linear regression analysis gives

$$\frac{[H^+]}{k_0[Pb^{2+}]^2} = \frac{1}{k_H^{CdCy}}\left(\frac{1 + K_{CdCyH}[H^+] + K_{CdCyPb}[Pb^{2+}]}{[Pb^{2+}]^2} + \frac{\beta_{CdCyPb_2}}{k_H^{CdCy}}\right) \quad (7)$$

$k_H^{CdCy} = 42.6$ and $\beta_{CdCyPb_2} = 6320$. Table II gives the equilibrium and kinetic constants and their standard deviations. The uncertainty for the value of K_{CdCyPb} is large but the data do not fit if this species is ignored.

Copper behaves in a manner similar to lead except that the copper complex with $CdCyDTA^{2-}$ is weaker and only one complex Cd(CyDTA)Cu appears to form, and an equation corresponding to eq 6 fits the data up to 0.20 M Cu^{2+}. Table II summarizes the rate constants and stability constants found for each exchange reaction. The constants for the Cu^{2+} and Pb^{2+} complexes are close to the values of the acetate complex of each $K_1 = 63$ and 129, respectively.[6] Direct evidence of the Cd(CyDTA)Pb and Cd(CyDTA)Cu complexes was noted from absorbance jumps when the reactants were mixed. However, the absorbance increases were small and not very suitable for determination of the stability constants of these species.

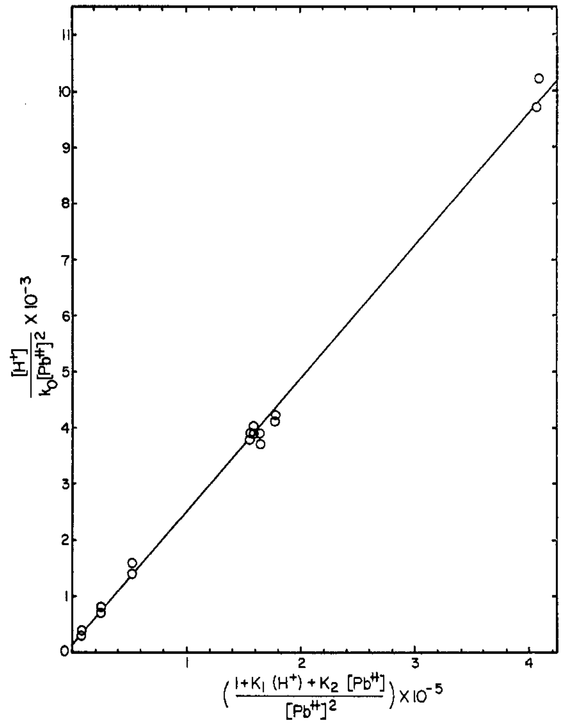

Figure 2.—Plot of eq 7 in order to resolve the stability constants of the lead complexes of $CdCyDTA^{2-}$. The reciprocal of the slope is k_H^{CdCy} and the intercept is $\beta_{CdCyPb2}/k_H^{CdCy}$. $K_1 = K_{CdCyH}$ and $K_2 = K_{CdCyPb}$.

TABLE II

CONSTANTS FOR THE REACTION MECHANISM IN EQ 2[a]

Stability constants, M^{-1}	Rate constants, M^{-1} sec^{-1}
$K_{CdCyPb} = 136 \pm 14$ $K_{CdCyPb_2} = 50 \pm 60$	$k_H^{CdCy} = 42.6 \pm 0.3$
$K_{CdCyCu} = 58 \pm 9$	$k_H^{CdCy} = 40.1 \pm 0.7$

[a] At 25° and $\mu = 0.1$.

TABLE III

EFFECT OF ACETIC ACID–ACETATE BUFFER ON THE OBSERVED RATE CONSTANT AT 25.0° AND $[Pb^{2+}{}_{total}] = 0.003$ M

Total acetate, M	pH	k_0, sec^{-1}
None	5.0	2.6×10^{-4}
0.02	5.08	3.3×10^{-4}
0.02	5.13	3.3×10^{-4}
0.10	4.79	9.8×10^{-4}
0.10	4.79	10.4×10^{-4}
0.50[a]	4.86	10.6×10^{-4}
None	4.13	2.2×10^{-3}
~0.01	4.10	3.5×10^{-3} [b]
0.10	4.07	4.3×10^{-3}
0.10	4.08	4.2×10^{-3}

[a] All other reactions were at $\mu = 0.10$ M. [b] This value is interpolated from rate constants at pH 3.7–4.3 with total acetate 0.006–0.013 M.

The value of k_H^{CdCy} can be predicted from the reversible kinetics in eq 8 using $k_{Cd}^{HCy} \simeq k_{Cd}^{HY}$ (the

$$CdCyDTA^{2-} + H^+ \underset{k_{Cd}^{HCy}}{\overset{k_H^{CdCy}}{\rightleftharpoons}} HCyDTA^{3-} + Cd^{2+} \quad (8)$$

value is 8.5×10^8 M^{-1} sec^{-1} for EDTA[7]) and log $K_{HCy} = 12.35$ and log $K_{CdCy} = 19.88$.[8] The predicted value is 25 M^{-1} sec^{-1}, which, considering the approximation, is in good agreement with the value of 40–42 M^{-1} sec^{-1} found in this work.

Acetic Acid–Acetate Acceleration.—When reaction 1 takes place in the presence of acetate buffer, the exchange rate is faster. Even at 0.003 M total acetate the k_0 values are 15–30% greater and at higher acetate concentrations the observed rate constants are 50–

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(6) N. Tanaka and K. Kato, *Bull. Chem. Soc. Japan*, **33**, 417, 1412 (1960).

(7) J. Koryta and Z. Zabransky, *Collection Czech. Chem. Commun.*, **25**, 3153 (1960).

(8) G. Anderegg, *Helv. Chim. Acta*, **46**, 1833 (1963).

100% larger. The buffer has at least two effects: (1) the acetate ion complexes Pb(II) reducing the effect of Pb(II) suppression and (2) the acetic acid acts as a general acid catalyst with $k_{\mathrm{HAc}}^{\mathrm{CdCy}} \simeq 5 \times 10^{-3}\ M^{-1}$ sec^{-1}. As shown in Table III the acetate reduction of the Pb(II) suppression is the larger effect as can be seen for the data at pH 5. The acetic acid acceleration is more important at pH 4 but is still a minor contribution to k_0. There may be additional effects but they were not sorted out.

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A Dipole Moment Study of Six-Coordinate Organotin Chelate Compounds

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Diphenyl-, dimethyl-, diethyl-, and dibutyltin acetylacetonates, dibenzoylmethanates, and hexafluoroacetylacetonates have been synthesized, and their structures have been studied in benzene and cyclohexane solutions. Polarization measurements obtained at several temperatures show that the complexes possess orientation dipole moments of 2.0–4.0 D. It appears likely that the molecules possess structures of the *cis*-octahedral type with most exhibiting some distortion from the regular geometry. The distortion appears to vary regularly with the electronegativities of the organic substituents. Supplementary infrared, ultraviolet, and nmr data, respectively, are consistent with the assumptions (1) that the complexes are six-coordinate, (2) that tin–oxygen bonds are of a simple polar type lacking (p → d)π character, and (3) that exchange is very rapid at room temperature for the β-ketoenolate groups.

Introduction

Several groups of workers[1-5] in the past few years have prepared neutral organotin complexes of the type R_2SnCh_2. The organic substituent, R, apparently can be either an alkyl or an aromatic group while the ligand, Ch^-, can be one of a variety of bidentate types possessing oxygen or nitrogen donor atoms. In prior work the complexes studied have been shown to be monomeric and six-coordinate.[1,2] An extensive structural study[1] of bis(2,4-pentanedionato)dimethyltin(IV) and several closely related compounds has indicated that only one of three possible isomers, the *trans* (D_{2h}), is stable in benzene and chloroform solutions. A very recent X-ray study[6] of bis(8-quinolinolato)dimethyltin(IV), on the other hand, points to the stability of a distorted *cis*-type structure for that molecule.

Most evidence accumulated[1,2] using physical techniques is consistent with the assignment of *trans* structures to phenyl and methyl derivatives, but the same evidence is not basically inconsistent with the assignment of structures of lower symmetry. For instance, the observation[2] that bis(2,4-pentanedionato)diphenyltin(IV) is not resolved upon passing in solution through a *d*-lactose column is consistent with the assignment of a *trans* structure. Yet a *cis*-type molecule would behave in similar fashion if rates of racemization were rapid enough to result in the loss of optical activity. The fact that chloroform solutions of bis(2,4-pentanedionato)dimethyltin(IV) exhibit only two methyl proton nmr peaks with areas under them showing a ratio of 2:1 can be explained in terms of a *cis* structure characterized by a rapid rate of ligand exchange as well as a *trans* structure. Infrared spectral data are hardly definitive since spectra of acetylacetonate complexes have been shown to be very similar regardless of structure. The Raman spectra[1] provide the most convincing argument in favor of the *trans* structure of bis(2,4-pentanedionato)dimethyltin(IV) since lines have been observed corresponding to both Sn–C and Sn–O symmetrical stretching vibrations. Yet, the totally symmetrical C–O vibration expected to be Raman active is missing in the above compound. Bis(2,4-pentanedionato)diphenyltin(IV) in solution has been shown[2] to exhibit large values of the polarization which could be due to an orientation dipole moment of 3.9 D or to a very large value of the atomic polarization.

The large polarization value is worth further investigation since dielectric constant measurements over a temperature range should clearly allow the distinction to be made between true orientation polarization and atomic polarization. A zero value of the dipole moment would be strong evidence for a *trans* (D_{2h}) structure. To determine the structures of molecules of the type R_2SnCh_2 a number of compounds have been synthesized and their electronic and total polarizations have been measured in solution.

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(1) M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).

(2) W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 89 (1965).

(3) R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.* (Amsterdam), **4**, 237 (1965).

(4) R. Barbieri, G. Faroglia, M. Gustiniani, and L. Roncucci, *J. Inorg. Nucl. Chem.*, **26**, 203 (1964).

(5) L. Roncucci, G. Faroglia, and R. Barbieri, *J. Organometal. Chem.* (Amsterdam), **1**, 427 (1964).

(6) E. O. Schlemper, *Inorg. Chem.*, **6**, 2012 (1967).