Mass Spectra of Metal Chelates. I. Substituent Effects on Ionization Potentials and Fragmentation Patterns of Some 1-Methyl-3-alkyl-1,3-dione–Copper(II) Chelates

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Abstract: The mass spectra of a series of bis(β-ketoenolate) complexes of copper(II), as well as bis(2,2-dimethyl-3,5-hexanedionato)zinc(II) and bis(2,2-dimethyl-3,5-hexanedionato)magnesium(II), show the same preferential fragmentation pattern, the most striking characteristic being the stepwise removal of the alkyl substituents. The populations of the species arising from this fragmentation process vary and can be rationalized on the basis of the electronic effects of the alkyl substituents; the ionization potentials of the copper chelates also reflect this trend. In all of these spectra a reaction of the chelate within the mass spectrometer, apparently a substitution of Cu by Fe, is observed under a variety of conditions.

Few reports dealing with the mass spectra of metal chelates have appeared in the literature.[4–8] This work attempts to establish a relationship between the electronic structure and the mass spectra of the copper(II) chelates of some 1,3-diones, through consideration of ion intensities and electron-impact ionization potentials[9] of systematically substituted compounds. The 1,3-dionatocopper(II) chelates have a wide range of thermodynamic stabilities and are suited to a study of this sort.

One of the striking features of the spectra (Table I) of the copper(II) chelates is the large number of fragments containing copper. These are easily identified because the naturally occurring isotopes of copper, ^{63}Cu and ^{65}Cu, are present in nearly a 2:1 ratio. The chelates studied appear to have a common preferential fragmentation pattern and to have three copper-containing species in common: m/e 231–233 (c), m/e 147–149 (g), and m/e 105–107 (h). The sum of the intensities of the m/e 231 and m/e 233 ions is reported as 100% in all cases so that the spectra may be easily compared.

Examination of the data for the copper species shows a clear pattern for the fragmentation process involving the stepwise elimination of the alkyl groups around the periphery of the chelate ring structure. As the stability of the radical formed from the alkyl group increases [$CH_3 < CH_2CH_3 < CH(CH_3)_2 < C(CH_3)_3$], the population of copper species containing that alkyl group decreases. In other words, the cleavage of t-butyl is a

favored process and copper species containing this group are least populous (Scheme I).[10] Also the loss of two methyl groups to give i is not observed, except in the trivial case where R is CH_3. The over-all fragmentation process for the copper-containing species is shown in Scheme I.

Scheme I. Fragmentation of Copper-Containing Species
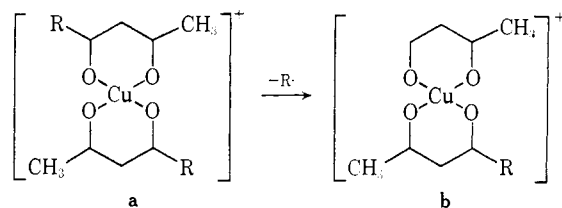
	R	m/e	Rel inten		m/e	Rel inten
1a	CH_3	261–263	216	1b	246–248	120
2a	CH_2CH_3	289–291	100	2b	260–262	105
3a	$CH(CH_3)_2$	317–319	42	3b	274–276	75
4a	$C(CH_3)_3$	345–347	17	4b	288–290	44
5a	CF_3	369–371	107	5b	300–302	90
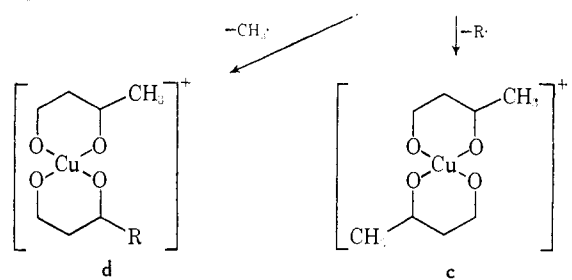
	m/e	Rel inten
1d	231–233	100
2d	245–247	20
3d	259–261	3
4d	273–275	1
5d	285–287	31

	m/e	Rel inten
	231–233	100
	common to each chelate	

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(4) F. W. McLafferty, Appl. Spectry., 11, 148 (1957).
(5) J. S. Shannon and J. M. Swan, Chem. Commun., 33 (1965).
(6) C. G. Macdonald and J. S. Shannon, Aust. J. Chem., 19, 1545 (1966), and references contained therein.
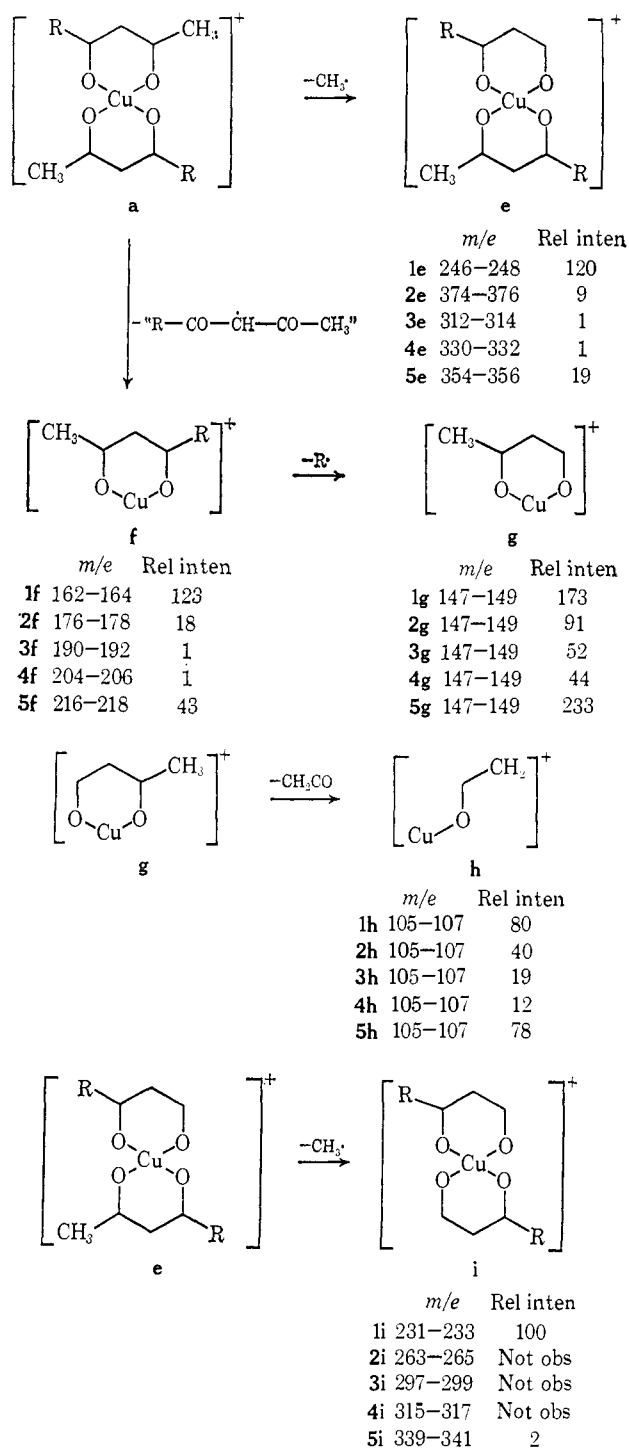(7) E. P. Dudek and M. Barber, Inorg. Chem., 5, 375 (1966); E. P. Dudek and G. O. Dudek, Inorg. Nucl. Chem. Letters, 2, 53 (1966).
(8) S. Sasaki, Y. Itagaki, T. Kurokawa, K. Nakanishi, and A. Kasahara, Bull. Chem. Soc. Japan, 40, 76 (1967), and references contained therein.
(9) The ionization potentials of a series of metal acetylacetonates are in disaccord with the prediction of theory: (a) G. M. Bancroft, C. Reichert, and J. B. Westmore, Inorg. Chem., 7, 870 (1968); (b) S. M. Schildcrout, R. G. Pearson, and F. E. Stafford, J. Am. Chem. Soc., 90, 4006 (1968).

(10) Alkyl losses crudely parallel intensities expected from consideration of the radical ionization potentials; attempts at a strict correlation, as attempted recently for purely organic systems,[11] are impossible because the primary processes of decomposition do not give identical ions.
(11) M. M. Bursey and E. S. Wolfe, Org. Mass Spectrom., 1, 543 (1968).

Scheme I (*Continued*)

	m/e	Rel inten
1e	246–248	120
2e	374–376	9
3e	312–314	1
4e	330–332	1
5e	354–356	19

	m/e	Rel inten
1f	162–164	123
2f	176–178	18
3f	190–192	1
4f	204–206	1
5f	216–218	43

	m/e	Rel inten
1g	147–149	173
2g	147–149	91
3g	147–149	52
4g	147–149	44
5g	147–149	233

	m/e	Rel inten
1h	105–107	80
2h	105–107	40
3h	105–107	19
4h	105–107	12
5h	105–107	78

	m/e	Rel inten
1i	231–233	100
2i	263–265	Not obs
3i	297–299	Not obs
4i	315–317	Not obs
5i	339–341	2

Another feature of the spectra is the presence of a copper species **g** that contains only one ligand minus the alkyl group. It may arise through Cu–O bond scission in **c**, and may be followed by cleavage to the interesting copper–ketene species **h**.

In both **c** and **h** the copper has apparently been reduced and is present as copper(I). If, on the other hand, the positive charge is completely localized on the copper atom, the formal oxidation state of copper would still be +2. The copper–ketene species **h** may give rise to copper(I) ion, which is observed in all cases; no copper(II) is observed.

The very low abundance of copper(I) ion can be rationalized on the basis of the strength of the Cu–O bonds as a result of the hyperconjugative effect of the alkyl group, which increases the electron density at the oxygens. As a verification of this explanation for the low intensity of copper(I) ion, the mass spectrum of bis(hexafluoroacetylacetonato)copper(II) (**6**) was determined. The strong electron-withdrawing effect of the trifluoromethyl groups is known to decrease the strengths of the Cu–O bonds, and this fact is reflected in the thermodynamic stability of the chelate.[12] As expected, copper(I) ion is a major fragment in the spectrum of bis(hexafluoroacetylacetonato)copper(II).

The mechanism of these fragmentation reactions is more difficult to formulate than those of simpler organic molecules because of the uncertain nature of the ligand–copper bonds. A formalized bond model is not meaningful inasmuch as formal bonds fail to point out the π-bonding possibilities that result from the quasi-aromatic nature of the chelate ring.[13]

The origin of the electron removed is of considerable interest, though the fragmentation patterns do not clarify this point. Whatever the orbital from which the electron is lost, energy is eventually localized sufficiently in the appropriate bonds so that one of two fragmentation paths is followed: (1) the parent ion can lose the alkyl groups one at a time, or (2) it can undergo ligand cleavage.[14] Pathway 1 would lead to the formation of other copper species in general, whereas pathway 2 could lead to fragments associated with the ligand in those cases where the ligand itself carries the charge after the fragmentation. Pathway 2 is apparently favored only if the organic species carries with it an extra hydrogen from some source, for the fragments characteristic of the dione itself are observed rather than those expected for the ligand as it exists in the chelate. The major fragments arising from ligand cleavage are listed in Table I and are typical of those reported for 1,3-diketones.[15]

A further question concerns the mechanism of the stepwise cleavage of the alkyl groups from the parent ion. This would seem to call for the transfer of an electron from one-half of the chelate structure to the other through the central copper atom, thereby allowing the alkyl groups to leave as radicals. Although valence-bond pictures can be used in mechanisms to depict plausible electron transfers in the ion, these are too speculative at the present to warrant presentation here.

The ionization potentials of these compounds reflect a similar effect of the substituent on the orbital from which the electron is removed. Table II lists values showing a substituent effect on ionization potential apparently as large as that found in substituted benzenes, where the ionization potential of trifluoromethylbenzene is 9.68 eV,[16] that of toluene is 8.82 eV,[16] and that of *t*-butylbenzene is 8.68 eV.[17]

(12) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953).

(13) J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *ibid.*, **83**, 531 (1961).
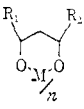
(14) An example of the stepwise cleavage of the ligand is given by McLafferty.[4]

(15) J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, **31**, 1384 (1966).

(16) L. D. Isaacs, W. C. Price, and R. G. Ridley, "The Threshold of Space," M. Zelikoff, Ed., Pergamon Press, Ltd., London, 1957, p 143.

(17) W. C. Price, R. Bralsford, P. V. Harris, and R. G. Ridley, *Spectrochim. Acta*, **14**, 45 (1959).

Table I. Mass Spectra of Chelates

	1 R₁ = CH₃, R₂ = CH₃, M = Cu, n = 2		2 R₁ = CH₃, R₂ = CH₂CH₃, M = Cu, n = 2		3 R₁ = CH₃, R₂ = CH(CH₃)₂, M = Cu, n = 2		4 R₁ = CH₃, R₂ = C(CH₃)₃, M = Cu, n = 2		5 R₁ = CH₃, R₂ = CF₃, M = Cu, n = 2	
	m/e	Rel inten	m/e	Rel inten	m/e	Rel inten	m/e	Rel inten	m/e	Rel inten
	27	62	27	25	27	6	27	4	43	300
	28	19	29	33	29	2	29	2	63, 65	70
	29	49	43	117	43	42	43	8	69	160
	43	885	57	47	63, 65	5	57	7	85	169
	58	40	63, 65	12	69	3	63, 65	2	105, 107	78
	72	51	69	8	71	4	85	21	119	20
	85	450	85	98	85	41	105, 107	12	139	34
	100[a]	365	99	21	105, 107	19	142[a]	3	147, 149	233
	105, 107	80	105, 107	39	128[a]	13	147, 149	44	154[a]	50
	147, 149	173	114[a]	52	147, 149	52	161, 163	3	159	20
	155	35	147, 149	91	161, 163	4	175, 177	2	201, 203	36
	161, 163	123	161, 163	6	175, 177	4	231, 233	100	216, 218	43
	175, 177	12	175, 177	35	231, 233	100	281	4	231, 233	100
	231, 233	100	231, 233	100	267	5	288, 290	44	285, 287	31
	239	22	245, 247	20	274, 276	75	338[b]	6	293	7
	246, 248	120	253	8	310[b]	8	345, 347[c]	16	300, 302	90
	254[b]	33	260, 262	105	317, 319[c]	41			327, 329	75
	261, 263[c]	216	274, 276	9					354, 356	19
			282[b]	14					362[b]	23
			289, 291[c]	100					369, 371[c]	107

[a] A representative intensity for the molecular ion of the 1,3-dione. [b] A representative intensity for the iron(II) chelate molecular ion.

The electronic effect of the substituent unsymmetrically disposed on the chelate ring is thus very large. If the charge is localized in one ring, the sensitivity to substituents parallels the sensitivity in another six-membered ring, benzene; if, on the other hand, the ionization potential reflects substitution in both rings, then the sensitivity to a single substitution would be only half as great as the effect of a single substitution on the benzene ring. To make a choice between these hypotheses, the ionization potentials of two compounds each containing two methyl and two trifluoromethyl groups on the quasi-aromatic rings were measured. One of these compounds is bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II) (5) (see Table I). The other is 2,4-pentanedionato-1′,1′,1′,5′,5′,5′-hexafluoro-2,4-pentanedionatocopper(II) prepared in the inlet system of the mass spectrometer by ligand exchange between the two symmetrical chelate compounds 1 and 6. If the ionization potential of the compound is affected by the entire system, both of these compounds should have very nearly the same ionization potential. But if one ring dominates the

orbital from which the electron is removed (e.g., if the electron is removed from a single chelate ring), the second compound should have an appreciably lower ionization potential than the first, because the electron should preferentially be removed from the chelate ring with greater electron density. The mixed-ligand compound should then have an ionization potential resembling that of bis(2,4-pentanedionato)copper(II) (1), perhaps slightly raised by an inductive effect of the ring bearing the trifluoromethyl groups.

The comparison of the ionization potentials for these two compounds supports the first picture, for the potentials are within the statistical error in reproducibility of our data. The energy of the orbital from which the electron is removed is controlled about equally by substituents in both rings. The scale of individual substituent effects is therefore actually about half that of the scale for ionization potential variation in substituted benzenes unless a nonequilibrium situation obtains in which the electron ionizes the ring which it affects first, irrespective of differences in ionization potentials.

6 $R_1 = CF_3$ $R_2 = CF_3$ $M = Cu$ $n = 2$		7 $R_1 = CH_3$ $R_2 = C(CH_3)_3$ $M = Zn$ $n = 2$		8 $R_1 = CH_3$ $R_2 = CH(CH_3)_2$ $M = Mg$ $n = 2$		9 $R_1 = CH_3$ $R_2 = CH_3$ $M = Cr$ $n = 3$	
m/e	Rel inten	m/e	Rel inten	m/e	Rel inten	m/e	Rel inten
28	3	28	2	28	3	28	2
63, 65	45	29	9	29	10	43	8
69	100	39	6	39	8	50, 52, 53, 54	7
75	6	41	20	41	17		
91	8	43	63	43	100		
104, 106	8	44	9	44	24	100ᵃ	1
119	9	57	35	57	6	108	4
139	38	85	83	71	9		
169	4	142ᵃ	8	85	97	149, 151, 152, 153	60
201, 203	108	148, 150, 151, 152	17	128ᵃ	21		
208ᵃ	3	205, 207, 208, 209, 247, 249	29	151, 152, 153	16	168	10
213	21	250, 251	6	183	6	248, 250, 251, 252	100
339, 341	27	281	6	235, 236, 237	48		
401	5	289, 291, 292, 293	100	267	2	347, 349ᶜ, 350, 351	17
408, 410	38	338ᵇ	3	278ᶜ, 279, 280	14		
470ᵇ	6	346, 348ᶜ, 349, 350	11	310ᵇ	4		
477ᶜ, 479	17						

ᶜ Molecular ion of chelate.

Table II. Ionization Potentials of Copper Chelates

Compd	Ring substituent		Ionization potential,ᵃ eV	No. of detns
1	CH_3	CH_3	7.75 ± 0.05	12
2	CH_3	CH_2CH_3	7.68 ± 0.03	6
3	CH_3	$CH(CH_3)_2$	7.61 ± 0.06	6
4	CH_3	$C(CH_3)_3$	7.59 ± 0.05	6
5	CH_3	CF_3	8.61 ± 0.05	10
6	CF_3	CF_3	9.68 ± 0.01	6
	$\begin{cases} CH_3 \\ CF_3 \end{cases}$	$\begin{cases} CH_3 \\ CF_3 \end{cases}$ ᵇ	8.65 ± 0.01	3

ᵃ Standard deviation of results reported; not an indication of accuracy. ᵇ Mixed ligands.

The facility with which ligands may exchange from one copper to another suggests an explanation for other curious peaks found in many of these spectra as a set whose intensities are reproducible with respect to the intensities of other members of the set but vary with respect to the copper chelate spectrum. These are a set whose molecular ion corresponds to a mass of (M −

63 + 56) in every case, where M represents the mass of the molecular ion containing ^{63}Cu. These are proposed to be ions corresponding to the replacement of Cu by Fe in the source or inlet[18] of the mass spectrometer. Our assignment is based on the following observations.

(1) In several spectra examined, a peak at m/e (M − 2) with intensity relative to M, the molecular ion, equal to 6.7 ± 0.15 % was found. In the spectrum of bis(2,4-pentanedionato)iron(II) an (M − 2) peak of intensity 6.7 % was also observed. The contribution of ^{54}Fe to the natural isotopic abundance of iron is responsible for most of this; the calculated value is 6.45 % for the ^{54}Fe contribution.

(2) High-resolution study of the (M − 63 + 56) peak in the spectrum of bis(2,4-pentanedionato)copper(II)

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Table III. Effect of Repeller Voltage on Chelate Exchange

m/e	1 Rel inten LRV[a]	1 Rel inten HRV[b]	m/e	2 Rel inten LRV	2 Rel inten HRV	m/e	3 Rel inten LRV	3 Rel inten HRV	m/e	4 Rel inten LRV	4 Rel inten HRV
239[c]	44	22	253[c]	95	8	267[c]	39	5	281[c]	63	4
246 248	105	120	260 262	92	106	274 276	56	75	288 290	39	44
254[c]	58	34	282[c]	109	15	310[c]	45	8	338[c]	64	7
261 263 [d]	151	216	289 291 [d]	76	100	317 319 [d]	27	42	345 347 [d]	17	17

[a] Low repeller voltage, 3 V. [b] High repeller voltage, 10 V. [c] Iron chelate. [d] Molecular ion of copper chelate.

shows it to be indistinguishable from $Fe(C_5H_7O_2)_2^+$ under conditions where purely organic species of low H content at the same nominal mass could be cleanly separated from the unknown ion.

(3) Ionization potentials for the iron compounds resemble those of the copper chelates, but are not identical: that for the supposed bis(2,4-pentanedionato)iron(II) is 7.50 ± 0.04 eV; for bis(1,1,1-trifluoro-2,4-pentanedionato)iron(II), 8.49 ± 0.03 eV; for bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)iron(II), 9.48 ± 0.07 eV; for 2,4-pentanedionato-1',1',1',5',5',5'-hexafluoro-2,4-pentanedionatoiron(II), 8.70 ± 0.04 eV. These values reflect the same magnitude of sensitivity to substituent effects as the copper compounds, and the values are far lower than those which might be expected for organic compounds not containing a large aromatic system.

The intensity of this set of peaks relative to peaks in the copper chelate spectrum varied with source conditions, particularly with repeller potential, as noted from Table III. This observation suggests that a large fraction of the replacement occurs in the source. Addition of a large excess of another gas (CO) did not significantly increase the amount of the $Fe(acac)_2^+$ produced. The spectra of bis(2,2-dimethyl-3,5-hexanedionato)zinc(II) (7) and bis(2-methyl-3,5-hexanedionato)magnesium(II) (8) also are contaminated with the same set of peaks. On the other hand, the spectrum of tris(2,4-pentanedionato)chromium(III) gave no discernible amount of the iron chelate. Whether there is an electronic or steric reason for this remains to be established. It is interesting that the effect so far has been noted only in square-planar complexes,[19] though the peaks also appear in the spectra of the acetylacetonates of sodium and lithium in very low abundance. These latter spectra are ill-defined, containing variable amounts of aggregates presumably resulting from the ionization of gaseous oligomers.

Experimental Section

Preparation of Compounds. The 1,3-diones were obtained from commercial sources or were synthesized by the method of Hauser.[20] The chelates were prepared by standard methods[21] and purified by vacuum sublimation.[22]

Mass Spectra. The spectra were recorded with either a Perkin-Elmer Hitachi RMU-6D double-focusing instrument at the Avery Laboratory or a Perkin-Elmer RMU-6E single-focusing instrument at the Venable Laboratory. Conditions for the former instrument were: ionizing voltage 80 eV, temperature of inlet 200°; those for the latter were: ionizing voltage 75 eV, temperature of inlet 190°. These instruments operate at an ionizing current of about 80 μA. Essentially identical spectra were obtained with sample introduction by the direct-insertion probe at room temperature. Variation of the temperature of the source between 60 and 200° did not alter the relative intensities of peaks in the spectra of selected compounds.

Electron-Impact Ionization Potentials. Extensive prior investigation indicated no improvement in the standard deviation for replicate determinations of ionization potentials by using an elaborate technique like the semilogarithmic plot method of Lossing, Tickner, and Bryce;[23] very similar means and deviations were found with Kiser and Gallegos's energy compensation technique,[24] which therefore formed the basis of our method. Several runs were performed for each compound, using xenon as a primary reference and benzene and anthracene as secondary references. Averages of recent literature electron-impact values for the references were taken as 12.12, 9.23, and 7.41 eV, respectively.[25] A correlation line through a plot of observed values for the standards against these values was used to establish the individual value for each chelate ionization potential. Data were recorded on different days and in some cases with different filaments. All data were obtained with the RMU-6E instrument at the Venable Laboratory which was modified to include a digital voltmeter (United Systems Corp., Dayton, Ohio) readable to ±0.01 V.

(19) The major fragmentation pathway of the chromium(III) chelate is the stepwise cleavage of the three ligands. This is in agreement with the earlier observation of McLafferty.[4]

(20) R. Levine, J. A. Conroy, J. T. Adams, and C. R. Hauser, J. Am. Chem. Soc., 67, 1510 (1945).

(21) J. T. Adams and C. R. Hauser, ibid., 66, 1220 (1944).

(22) R. L. Lintvedt, H. D. Russell, and H. F. Holtzclaw, Jr., Inorg. Chem., 5, 1603 (1966).

(23) F. P. Lossing, A. W. Tickner, and W. A. Bryce, J. Chem. Phys., 19, 1254 (1951).

(24) R. W. Kiser and E. J. Gallegos, J. Phys. Chem., 66, 947 (1962).

(25) Cf. R. W. Kiser, "Tables of Ionization Potentials," TID-6142, U. S. Department of Commerce, Washington, D. C., June 20, 1960, and supplements thereto.