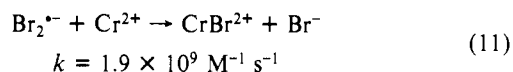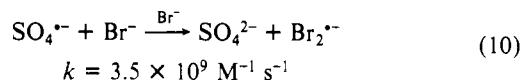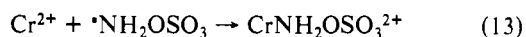increases only to 22%. Thus in the experiments with no added sulfate the reaction sequence shown in eqs 8 and 9 can account for only a small fraction of the $CrSO_4^+$ found.

The proposed reaction scheme is strongly supported by the results of the trapping experiments with Br^-. The sulfate radical anion reacts rapidly with Br^- to yield $Br_2^{\cdot-}$ (eq 10).[16] The

$$SO_4^{\cdot-} + Br^- \xrightarrow{\text{Br}^-} SO_4^{2-} + Br_2^{\cdot-} \tag{10}$$
$$k = 3.5 \times 10^9 \ M^{-1} \ s^{-1}$$

$$Br_2^{\cdot-} + Cr^{2+} \rightarrow CrBr^{2+} + Br^- \tag{11}$$
$$k = 1.9 \times 10^9 \ M^{-1} \ s^{-1}$$

reduction of $Br_2^{\cdot-}$ by Cr^{2+} (eq 11) yields $CrBr^{2+}$,[17] which can be easily identified by its visible spectrum. The formation of large amounts of $CrBr^{2+}$ in the reaction of HSA with Cr^{2+} in the presence of free bromide is thus a strong indiciation that $SO_4^{\cdot-}$ was produced in the reaction.[12]

The species that we assigned the composition $CrNH_2OSO_3^{2+}$ is a minor product. The most obvious route to it, namely reactions 12 and 13, can probably be ruled out on the basis of the spec-

$$SO_4^{\cdot-} + NH_2OSO_3H \rightarrow HSO_4^- + \cdot NH_2OSO_3 \tag{12}$$

$$Cr^{2+} + \cdot NH_2OSO_3 \rightarrow CrNH_2OSO_3^{2+} \tag{13}$$

trophotometric titrations, which yielded the same stoichiometric ratio of 1.92, irrespective of the order of addition of the two reactants. The sequence of reactions 1, 12, and 13 should have a 1:1 stoichiometry, and it should contribute to the overall reaction most significantly when HSA is present in excess, i.e., in the early stages of titrations with Cr^{2+}. No deviations from linearity were ever observed in any of the titrations.[18] Although the experimental stoichiometric ratio is not precisely 2.0, the deviation is too small to have any mechanistic significance.

It is possible that small amounts of $Cr(NH_2OSO_3)^+$ exist in reaction solutions. Oxidation of this species by $SO_4^{\cdot-}$ or by HSA may account for the observed product.

Both one-electron and two-electron[11] reactions of HSA/SA^- take place by the initial attack at the nitrogen. Since the steric

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(16) Redpath, J. L.; Willson, R. L. *Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* **1975,** *27,* 389.
(17) Laurence, G. S.; Thornton, A. T. *J. Chem. Soc., Dalton Trans.* **1974,** 1142.
(18) Note that reactions 12 and 13 would not affect the kinetics in the presence of excess HSA, despite the change in stoichiometry. This is due to the fact that for each rate-determining step 2 equiv of the limiting reagent, Cr^{2+}, would still be consumed.

crowding at this site does not seem dramatically different from that at the oxygens, the preference for nitrogen must be caused by electronic factors. As mentioned earlier,[11] the anion OSO_3H^- is an exceptionally good leaving group. This explains the unusually high reactivity of HSA in nucleophilic substitutions. For example, cob(I)alamin reacts with HSA >5 × 10^3 times faster than with NH_3OH^+. However, the one-electron reductant Cr^{2+} reacts with $SA^- \sim 10^3$ times more rapidly than with NH_3OH^+ ($k = 0.014$ M^{-1} s^{-1}).[1] It is difficult to comment on the relative stabilities of the two radicals, $SO_4^{\cdot-}$ and $NH_2^{\cdot}/NH_3^{\cdot+}$, produced in these reactions. However, other factors, such as the one-electron-reduction potentials of the parent molecules, must play a crucial role in determining their reactivity toward Cr^{2+}. Our data suggest that $NH_2OSO_3^-$ is a more reactive one-electron oxidant than NH_3OH^+.

We have no new experimental results to offer concerning the reaction[9,10] of Fe^{2+} with HSA. In view of the aminations caused by this reaction, however, we suggest that either the mechanism for Fe^{2+} changes compared to that for Cr^{2+}, producing an active $\cdot NH_2/\cdot NH_3^+$ radical, or the species $FeNH_3^{3+}$ (analogous to $CrNH_3^{3+}$) is itself an aminating agent. Of course the iron(II) mechanism may change even more drastically, and a two-electron process remains yet another possibility.

Experimental Section

Solutions of $Cr(ClO_4)_2$ were prepared by reduction of solutions of hexaaquochromium(III) over zinc amalgam. Hydroxylamine-*O*-sulfonic acid (Aldrich) was used as received.

Products were separated aerobically by ion-exchange chromatography using SP-Sephadex C-25 resin. The acidity of the eluent was increased in 0.1 M increments until all products bearing ≤3+ charge were removed from the column. The products Cr^{3+}, $CrNH_3^{3+}$, $CrBr^{2+}$, and $CrSO_4^+$ were identified by visible spectroscopy.[13,19]

The kinetics were monitored at 394 and 545 nm by use of a Cary 219 spectrophotometer. All kinetic experiments were conducted under pseudo-first-order conditions at 25.0 ± 0.2 °C. Anaerobic conditions were maintained throughout. Lithium perchlorate was used as the supporting electrolyte to maintain ionic strength at 1.0 M. Data were analyzed by standard procedures.

The acidity constant of HSA was determined by measuring the pH of solutions containing different concentrations of HSA (0.015–0.15 M) in 1.0 M LiClO$_4$. Some of the solutions were partly neutralized with a standard solution of NaOH. The electrode was standardized against solutions of 0.1 and 0.01 M HClO$_4$ in 1.0 M LiClO$_4$.

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(19) Taube, H.; Myers, H. *J. Am. Chem. Soc.* **1954,** *76,* 2103.

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Stability of Metal Ion Unsubstituted and Substituted Monocarboxylate Complexes in Aqueous Solutions

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Summarized results obtained in this laboratory on the stability of 90 metal ion complexes with unsubstituted and substituted monocarboxylate ligands, published elsewhere, have been analyzed. The contribution of ligand basicity, chelating effect, and metal ion order of stability are quantitized in order to give better insight into the stability of this class of weak coordinative interactions between metal ion and ligands. The special value of this analysis lies in the fact that all systems have been investigated with at least two independent physicochemical methods using identical or close to identical experimental conditions such as $t = 25$ °C and $I = 2$ mol/L (NaClO$_4$), but the same procedure can be used for any class of coordination compounds if reliable data on their stability are available.

Introduction

The factors governing the stability of coordination compounds formed between a metal ion and organic ligands are quite complex. Despite the advances in theoretical chemistry, at the present time,

it is not possible to calculate the stability constants of a given compound from strictly theoretical considerations. Therefore, the correlation of the stability constants with respect to different metal ions and/or ligands with identical experimental conditions usually

Table I. Abbreviations for Anions of Unsubstituted and Substituted Monocarboxylic Acids Used as Ligands in This Investigation

Unsubstituted Monocarboxylates
FORM = formate
ACET = acetate
PROP = propionate or propanoate
BUTY = butyrate or butanoate

Substituted Monocarboxylates
CLAC = 2-chloroacetate
CNAC = 2-cyanoacetate
PHAC = 2-phenylacetate
GLYCO = glycolate or 2-hydroxyacetate
MAND = mandelate or 2-phenyl-2-hydroxyacetate
PYRU = pyruvate or 2-oxopropionate or 2-oxopropanoate
LACT = lactate or 2-hydroxypropionate or 2-hydroxypropanoate
3OHP = 3-hydroxypropionate or 3-hydroxypropanoate
GLYCE = glycerate or 2,3-dihydroxypropionate or 2,3-dihydroxypropanoate
2OHB = 2-hydroxybutyrate or 2-hydroxybutanoate
3OHB = 3-hydroxybutyrate or 3-hydroxybutanoate
4OHB = 4-hydroxybutyrate or 4-hydroxybutanoate

Table II. pK Values of Conjugated Acids of Investigated Monocarboxylate Ligands obtained by Potentiometric Measurements at t = 25.0 ± 0.1 °C and I = 2 mol/L (NaClO₄) and Compared with Literature Data

	pK		
ligand	this work	ref 37	ref 38
FORM	3.86	3.75	3.75
ACET	4.74	4.75	4.76
PROP	4.88	4.87	4.87
BUTY	4.86	4.81[a]	4.82
CLAC	2.68[b]	2.85	2.86
CNAC	2.48	2.45	2.47
PHAC	4.34	4.28[a]	4.31
GLYCO	3.77	3.83	3.83
MAND	3.33	3.85	3.41
PYRU	2.27		
LACT	3.81	3.08[c]	3.86
3OHP	4.56	4.51	4.51
GLYCE	3.54		
2OHB	3.80		
3OHB	4.53	4.70	4.70
4OHB	4.85	4.72	4.72

[a] At 18 °C. [b] At 20 °C. [c] At 100 °C.

serves to determine the general factors involved in coordination of a given series of complex compounds.[1] Such a correlation is useful to understand the solution stability of complex compounds, as well as to predict the stability of some newly synthesized compounds having similar chemical properties.

In the present paper the stability constants of some metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}) and a series of some unsubstituted and substituted monocarboxylate anions, determined in this laboratory over many years and published elsewhere,[2-36]

have been summarized and analyzed. This analysis was made in order to give better insight into the factors governing the stability of this series of complex compounds and in order to quantitatively extract the contribution of each factor.

The quality of the experiments and the papers dealing with determination of stability constants for complex compounds varies greatly, and the same is true for even an easier task such as determination of dissociation constants for weak acids. Just a brief look into some of the handbooks[37-40] will prove this statement. An attempt was made to publish a handbook of only those stability constants that, according to selected experts seemed to be the most reliable,[41] but even this selection has only approximative value because the quality of measurements, data evaluation, etc. are obviously different from laboratory to laboratory.

Using only one method and one set of experiments and using very precise measurements and statistical data evaluation, it is possible to determine monoligand stability constants to 0.01 log K unit or even better. But when one is dealing with overall repeatability or when one is comparing the values obtained with different methods, according to the authors' experience, a difference of 0.05 log K unit is good agreement, while 0.10 log unit is still an acceptable difference. Therefore, the best way to investigate the stability constants of a series of complex compounds having similar chemical properties is to compare their stability constants determined with identical or almost identical experi-

(1) Lewis, J.; Wilkins, R. G. *Modern Coordination Chemistry*; Interscience Publishers Inc.: New York, 1960.
(2) Klemenčič, V.; Filipović, I. *Croat. Chem. Acta* **1958**, *30*, 99.
(3) Klemenčič, V.; Filipović, I. *Croat. Chem. Acta* **1958**, *31*, 3.
(4) Klemenčič, V.; Filipović, I. *Croat. Chem. Acta* **1958**, *31*, 23.
(5) Filipović, I.; Bujak, A.; Marač, M.; Novak, R.; Vukičević, V. *Croat. Chem. Acta* **1960**, *32*, 219.
(6) Filipović, I.; Piljac, I.; Crnič, Z.; Radulović, M.; Valenteković, Dj. *Croat. Chem. Acta* **1961**, *33*, 45.
(7) Medved, A.; Filipović, I. *Croat. Chem. Acta* **1963**, *35*, 51.
(8) Filipović, I.; Piljac, I. *Croat. Chem. Acta* **1964**, *36*, 181.
(9) Savič, J. S.; Filipović, I. *Croat. Chem. Acta* **1965**, *37*, 91.
(10) Filipović, I.; Piljac, I.; Medved, A.; Savič, S.; Bujak, A.; Bach-Dragutinović, B.; Mayer, B. *Croat. Chem. Acta* **1968**, *40*, 131.
(11) Topuzovski, B.; Filipović, I. *Croat. Chem. Acta* **1968**, *40*, 257.
(12) Grabarić, B.; Filipović, I. *Croat. Chem. Acta* **1970**, *42*, 479.
(13) Filipović, I.; Bujak, A.; Vukičević, V. *Croat. Chem. Acta* **1970**, *42*, 493.
(14) Filipović, I.; Matusinović, T.; Mayer, B.; Piljac, I.; Bach-Dragutinović, B.; Bujak, A. *Croat. Chem. Acta* **1970**, *42*, 305.
(15) Savič, J.; Savič, M.; Filipović, I. *Croat. Chem. Acta* **1972**, *44*, 305.
(16) Filipović, I.; Piljac, I.; Bach-Dragutinović, B.; Kruhak, I.; Grabarić, B. *Croat. Chem. Acta* **1973**, *45*, 447.
(17) Nushi, S.; Piljac, I.; Grabarić, B.; Filipović, I. *Croat. Chem. Acta* **1973**, *45*, 453.
(18) Piljac, I.; Grabarić, B.; Filipović, I. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *42*, 433.
(19) Grabarić, B.; Piljac, I.; Filipović, I. *Anal. Chem.* **1973**, *45*, 1932.
(20) Grabarić, B.; Mayer, B.; Piljac, I.; Filipović, I. *J. Inorg. Nucl. Chem.* **1974**, *36*, 3809.
(21) Grabarić, B.; Mayer, B.; Piljac, I.; Filipović, I. *Electrochim. Acta* **1975**, *20*, 799.
(22) Piljac, I.; Grabarić, B.; Tkalčec, M.; Školjoli, Š.; Filipović, I. *Croat. Chem. Acta* **1975**, *47*, 105.
(23) Grabarić, B.; Tkalčec, M.; Piljac, I.; Filipović, I.; Simeon, Vl. *Anal. Chim. Acta* **1975**, *74*, 147.
(24) Filipović, I.; Piljac, I.; Grabarić, B.; Mayer, B. *Anal. Chim. Acta* **1975**, *76*, 224.
(25) Grabarić, B.; Filipović, I. *Croat. Chem. Acta* **1976**, *48*, 17.
(26) Kruhak, I.; Grabarić, B.; Filipović, I.; Piljac, I. *Croat. Chem. Acta* **1976**, *48*, 119.
(27) Mayer, B.; Medančić, R.; Grabarić, B.; Filipović, I. *Croat. Chem. Acta* **1978**, *51*, 151.
(28) Filipović, I.; Bach-Dragutinović, B.; Ivičić, N.; Simeon, Vl. *Thermochim. Acta* **1978**, *27*, 151.
(29) Nushi, S.; Tkalčec, M.; Filipović, I.; Piljac, I. *Croat. Chem. Acta* **1979**, *52*, 17.
(30) Kruhak, I.; Filipović, I. *Croat. Chem. Acta* **1979**, *52*, 207.
(31) Medančić, R.; Kruhak, I.; Mayer, B.; Filipović, I. *Croat. Chem. Acta* **1980**, *53*, 419.
(32) Tkalčec, M.; Grabarić, B. S.; Filipović, I.; Piljac, I. *Anal. Chim. Acta* **1980**, *122*, 395.
(33) Matusinović, T.; Filipović, I. *Talanta* **1981**, *28*, 199.
(34) Filipović, I. *Kem. Ind.* **1980**, *30*, 369.
(35) Tkalčec, M.; Grabarić, B. S.; Filipović, I. *Anal. Chim. Acta* **1982**, *143*, 255.
(36) Matusinović, T.; Filipović, I. *Croat. Chem. Acta* **1985**, *58*, 227.
(37) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 65th ed.; CRC Press: Cleveland, OH, 1984.
(38) Nikolskij, B. P., Ed. *Spravočnik Himika*; Izdateljstvo Himija: Leningrad, USSR, 1971.
(39) Sillen, L. G., Martell, A. E., Eds. *Stability Constants of Metal-Ion Complexes*; The Chemical Society: London, 1964.
(40) Sillen, L. G., Martell, A. E., Eds. *Stability Constants of Metal Ion Complexes, Supplement No. 1*; The Chemical Society: London, 1971.
(41) Martell, A. E., Smith, R. M., Eds. *Critical Stability Constants*; Plenum Press: New York, 1977.

mental conditions using preferably two or more independent methods. The results obtained in such a way will also have some scattering, but it will be possible to extract the general trend because the eventual systematic error introduced by only one method will be minimized.

In this laboratory, the investigation of the stability of complexes between some metal ions and unsubstituted and substituted monocarboxylate ligand has been undertaken over many years. During this period, many improvements of the methods used in these investigations have been done. Measurements have evolved from those using commercially available instrumentation with limited accuracy and precision to those using highly accurate and precise homemade computerized instrumentation. Data evaluation has also evolved from graphical estimation to rigorous polynomial least-squares fitting procedures. Many different experimenters have been investigating the same systems, but regardless of all these differences a good to very good agreement is obtained, enabling the extraction and separation of the main factors governing the stability of the investigated systems.

The abbreviations used for investigated ligands are given in Table I. All the systems investigated form weak consecutive complexes, and therefore, they can be used as model systems for weak complex formation interactions.

Experimental Section

The experiments reported in this paper have been performed earlier so the experimental conditions and methods used are given in this section only briefly.

All the experiments have been carried out at a constant temperature of 25.0 ± 0.1 °C and an ionic strength of 2 mol/L obtained by addition of sodium perchlorate. The system with the chloroacetate ligand has been examined at $t = 18.0 \pm 0.1$ °C due to the slight tendency toward chloroacetate degradation at higher temperatures.

Three methods have been used for stability constant determination, i.e. potentiometric, polarographic, and spectrophotometric methods. Each system has been examined with at least two methods whenever possible.

Potentiometric determination of stability constants has been done by using improved Fronaeus' method.[42] The measurements have been carried out with either a precise potentiometric bridge in earlier papers or an automatic potentiometric titration apparatus or a homemade on-line computerized titration system[29] in later papers.

In polarographic experiments, the method of DeFord–Hume[43] has been used. Polarograms were recorded either on a manual polarograph in earlier papers or by using a computerized system built in this laboratory.[44]

Bjerrum's spectrophotometric method[45] of corresponding solutions, which is incidentally not used much in the literature, has been used because it was found to be the most suitable for stability constant determination of consecutive complex formations.

Values of stability constant were obtained either by using Leden's original graphical method[46] in earlier papers or by using a polynomial least-squares fitting procedure[17,18] in the later papers.

Results and Discussion

In comparing the stability of investigated metal ion complexes, the basicity of the ligand is estimated through the pK(HL) values of the corresponding conjugated acids.

In order to correlate ligand basicity (pK) with complex stability constants under the same experimental conditions, the pK values of investigated monocarboxylic acids have been determined potentiometrically. In Table II, these results are summarized and compared with data from some handbooks.[37,38] It can be seen that the agreement in most of the cases is very good, but some discrepancies have also been found, which are mainly due to different temperatures and/or ionic strengths.

According to our experience the most reliable stability constant, determined in a system of consecutive complex formation equilibria, is that of the monoligand complex. In Table III, log K(ML) values and the corresponding estimated errors of monoligand

(42) Fronaeus, S. *Acta Chem. Scand.* **1950**, *4*, 72.
(43) DeFord, D. D.; Hume, D. N. *J. Am. Chem. Soc.* **1951**, *73*, 5321.
(44) Tkalčec, M.; Filipović, I.; Piljac, I. *Anal. Chem.* **1975**, *47*, 1773.
(45) Bjerrum, J. *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd.* **1944**, *No. 4*, 21.
(46) Leden, I. *Z. Phys. Chem.* **1940**, *188A*, 160.
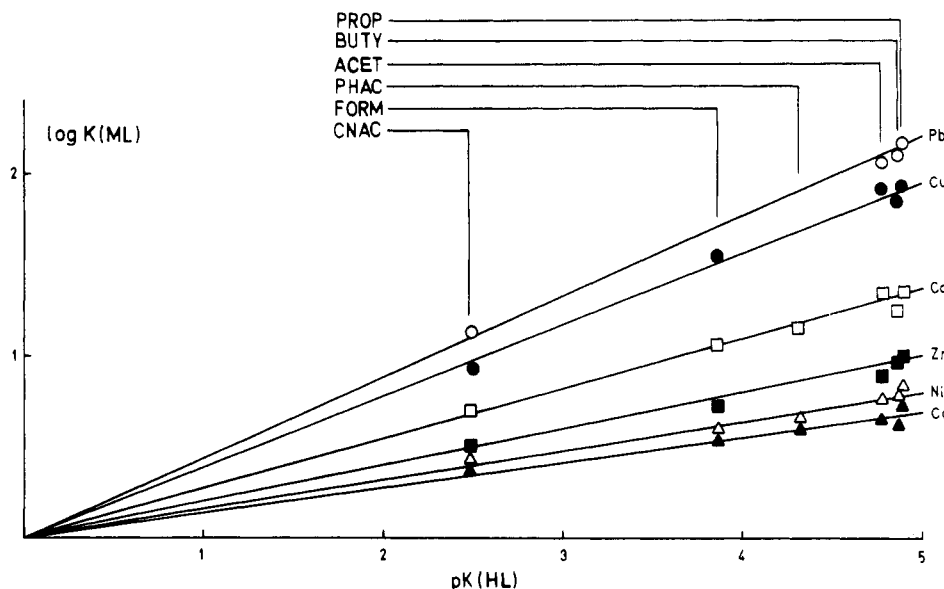(47) Grabarić, B. S. Unpublished results.

Table III. log K Values of Monoligand Stability Constants of the Investigated Unsubstituted Monocarboxylate Complexes of Metal Ions Obtained by Different Methods at $t = 25.0 \pm 0.1$ °C and $I = 2$ mol/L $(NaClO_4)^a$

metal ion	log K				method (ref)
	FORM	ACET	PROP	BUTY	
Co^{2+}	0.40 ± 0.05	0.61 ± 0.01	0.78 ± 0.01	0.61 ± 0.01	sp (12)
	0.73 ± 0.02	0.66 ± 0.04	0.70 ± 0.02	0.66 ± 0.01	pt (14)
	0.45 ± 0.01^b			0.59 ± 0.02	sp (19)
av	0.53 ± 0.03	0.64 ± 0.03	0.74 ± 0.02	0.62 ± 0.01	
Ni^{2+}	0.40 ± 0.06	0.82 ± 0.02	0.88 ± 0.03	0.81 ± 0.05	sp (12)
	0.66 ± 0.04	0.72 ± 0.02	0.73 ± 0.01	0.73 ± 0.01	pt (14)
	0.80 ± 0.01^b			0.71 ± 0.05	sp (19)
av	0.64 ± 0.04	0.77 ± 0.02	0.81 ± 0.02	0.75 ± 0.04	
Cu^{2+}	1.65 ± 0.05	2.00 ± 0.04	2.04 ± 0.04	1.90 ± 0.05	pl (7)
	1.40 ± 0.05	1.70 ± 0.04	1.60 ± 0.04	1.54 ± 0.08	pl (10)
	1.65 ± 0.06	2.12 ± 0.01	2.16 ± 0.01	2.08 ± 0.02	sp (12)
	1.59 ± 0.08	1.91 ± 0.01	1.94 ± 0.01	1.89 ± 0.02	sp (25)
av	1.57 ± 0.06	1.93 ± 0.03	1.94 ± 0.03	1.85 ± 0.04	
Zn^{2+}	0.60 ± 0.05	0.60 ± 0.06	0.90 ± 0.05	0.85 ± 0.06	pl (6)
	0.70 ± 0.06	1.04 ± 0.05	1.08 ± 0.05	1.00 ± 0.05	pl (10)
	0.70 ± 0.02	0.85 ± 0.03	1.00 ± 0.03	0.98 ± 0.05	pt (14)
	0.90 ± 0.02	1.10 ± 0.02^b		0.97 ± 0.01	pt (16)
av	0.73 ± 0.04	0.90 ± 0.04	0.99 ± 0.04	0.95 ± 0.04	
Cd^{2+}	1.30 ± 0.04	1.60 ± 0.05	1.48 ± 0.03	1.23 ± 0.05	pl (7)
	1.04 ± 0.03	1.30 ± 0.04	1.30 ± 0.03	1.30 ± 0.04	pl (10)
	0.85 ± 0.03	1.08 ± 0.03	1.23 ± 0.03	1.20 ± 0.03	pt (14)
av	1.06 ± 0.03	1.33 ± 0.04	1.34 ± 0.03	1.24 ± 0.04	
Pb^{2+}	1.11 ± 0.04	2.18 ± 0.04	2.23 ± 0.03	2.08 ± 0.04	pl (5)
	1.23 ± 0.03	2.15 ± 0.04	2.34 ± 0.04	2.08 ± 0.05	pl (10)
	1.11 ± 0.04	1.91 ± 0.03	2.07 ± 0.06	2.17 ± 0.06	pt (14)
			2.12 ± 0.03		pl (32)
			2.18 ± 0.03		vl (35)
av	1.15 ± 0.04	2.08 ± 0.04	2.19 ± 0.04	2.11 ± 0.05	

^{a} Abbreviations: av = average value of log K and standard errors; sp = spectrophotometric method; pt = potentiometric method; pl = polarographic method; vl = voltammetric method. In Tables III and V, log values of stability constants taken from ref 2–10 are given with estimated errors in graphical determinations, while those taken from ref 11 on are given with standard errors obtained from polynomial least-squares fitting. ^{b} Reference 47, potentiometric method.

stability constants obtained by different methods are presented, together with their average values. Despite the fact that all the results summarized do not have the same reliability, the general trend can be clearly seen.

The thermodynamic relationship between the stability constants of related monoligand and proton complexes can be derived from the corresponding standard partial molar free energies[51] as

$$\Delta G^{\ominus}(ML) =$$
$$\Delta G^{\ominus}(HL) + [G^{\ominus}(ML) - G^{\ominus}(HL)] + [G^{\ominus}(H) - G^{\ominus}(M)] \quad (1)$$

and substituting

$$\Delta G^{\ominus} = -2.3RT \log K^{\ominus} \quad (2)$$

one can obtain

$$\log K^{\ominus}(ML) = \log K_f^{\ominus}(HL) +$$
$$(1/2.3RT)\{[G^{\ominus}(M) - G^{\ominus}(H)] + [G^{\ominus}(HL) - G^{\ominus}(ML)]\} \quad (3)$$

where $K^{\ominus}(ML)$ and $K_f^{\ominus}(HL)$ refer to the standard formation constants of monoligand and proton complexes, respectively.

When the stabilities of complexes with different ligands for a given metal ion are compared, the term $[G^{\ominus}(M) - G^{\ominus}(H)]$ will be constant, and substituting

$$pK^{\ominus}(HL) = \log K_f^{\ominus}(HL) \quad (4)$$

one can obtain

$$\log K^{\ominus}(ML) =$$
$$pK^{\ominus}(HL) - (1/2.3RT)[G^{\ominus}(HL) - G^{\ominus}(ML)] + B \quad (5)$$

Figure 1. Linear relationship between log $K(ML)$ and pK(HL) for unsubstituted and substituted monocarboxylate ligands.

where p$K^{\ominus}$(HL) refers to the dissociation constant of the acid. If $[G^{\ominus}(HL) - G^{\ominus}(ML)] = 0$, then eq 5 can be written as

$$\log K^{\ominus}(ML) = pK^{\ominus}(HL) + B \qquad (6)$$

where the constant B can be associated with the logarithm of the proton displacement standard equilibrium constant for the following equilibrium (charges are omitted for simplicity):

$$M + HL \rightleftharpoons ML + H \qquad (7)$$
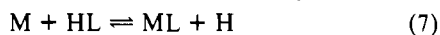
$$K^{\ominus} = a(ML)\, a(H)\, a(L)/[a(M)\, a(HL)\, a(L)] =$$
$$K^{\ominus}(ML)/K_f^{\ominus}(HL) \qquad (8)$$

$$\log K^{\ominus}(ML) = pK^{\ominus}(HL) + \log K^{\ominus} \qquad (9)$$

Therefore, if the linear relationship of log $K^{\ominus}$(ML) vs p$K^{\ominus}$(HL) is obtained showing a slope of approximately unity, then the approximation $[G^{\ominus}(HL) - G^{\ominus}(ML)] = 0$ will be valid. If, however, $[G^{\ominus}(HL) - G^{\ominus}(ML)]$ is a linear function of p$K^{\ominus}$(HL), i.e. if the dependence of $G^{\ominus}$(HL) with ligand is similar to that of $G^{\ominus}$(ML), then the slope of log $K^{\ominus}$(ML) vs p$K^{\ominus}$(HL) will not be unity, and the general relation will hold,[49] expressed this time in concentration stability constants using the constant ionic strength concept:

$$\log K(ML) = a\, pK(HL) + b \qquad (10)$$

The slope, a, in eq 10 can be found experimentally for a certain class of ligands and for different metal ions. It was found that this slope depends on the nature and properties of metal ions, and it has been suggested that it depends on the ionization potential of metal ion, on the nuclear repulsion between metal ion and electron donor atoms, and on the extent of polarization of the ligand by the metal ion.[1]

When the log K(ML) vs pK(HL) relationship for the investigated unsubstituted monocarboxylate complexes is analyzed, despite the narrow pK range and scattering of the results due to different methods and experimenters during relatively long period of investigation, a linear relationship was found, with a and b constants given in Table IV together with the linear regression correlation coefficients.

The y-axis intercepts, b, for the investigated systems statistically did not significantly differ from zero, so it was concluded that the scattering of the results (approximately 0.1 log K unit) is primarily responsible for this deviation. Therefore, another linear regression analysis was made including the origin. The new results are also shown in Table IV and in Figure 1.

The only exception strongly deviating from the general trend is the system with lead (II) formate complexes. This system gives a value of log K(ML) approximately 0.6 log K unit lower than that expected from the linear relationship. Such an unusual

Table IV. Linear Regression Coefficients for the log K vs pK Relationship Holding between Metal Ions and Unsubstituted Monocarboxylate Ligands[a]

metal ion	a	b	r	type of fitting
Co^{2+}	0.14 ± 0.07	−0.03 ± 0.33	0.821	A
	0.14 ± 0.01	0.00 ± 0.07	0.989	B
Ni^{2+}	0.16 ± 0.03	0.00 ± 0.33	0.958	A
	0.16 ± 0.03	0.00 ± 0.03	0.998	B
Zn^{2+}	0.23 ± 0.04	−0.15 ± 0.17	0.974	A
	0.20 ± 0.01	0.00 ± 0.04	0.998	B
Cd^{2+}	0.24 ± 0.07	0.12 ± 0.34	0.922	A
	0.27 ± 0.01	0.00 ± 0.07	0.997	B
Cu^{2+}	0.34 ± 0.07	0.26 ± 0.32	0.960	A
	0.39 ± 0.01	0.00 ± 0.08	0.998	B
Pb^{2+}	0.66 ± 0.45	−1.07 ± 2.16	0.828	A
	0.44 ± 0.01	0.00 ± 0.05	0.999	B

[a] Abbreviations: a = the straight line slope; b = the y-axis intercept; r = correlation efficient; A = no origin included; B = origin included.

behavior for this system is most likely due to the interaction of the relatively large Pb^{2+} ion and formate ligand which has a tendency toward association. This system, however, is still under very rigorous reexamination in this laboratory.

The stability constants of complexes with the same ligand and different metal ions increase in the order

$$Co^{2+} < Ni^{2+} < Zn^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}$$
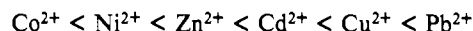
with corresponding incrase of the slopes, a, of the straight lines in Figure 1 and eq 10

$$0.14 < 0.16 < 0.20 < 0.27 < 0.39 < 0.44$$

This is in accordance with the well-known Irving–Williams order,[48] but for this class of complexes, it is for the first time quantitized through the values of the straight-line slopes.

All experimentally determined slopes of pK(HL) vs log K(ML) relationships have values smaller than unity. This fact can be explained by the already mentioned differences in the Gibbs' energy of metal ion and proton complexes which in turn also shows the different characters of metal ion–ligand and proton–ligand bonds. Partial molar Gibbs' energies of proton and metal ion complexes are similarly dependent on σ-donor properties of the carboxylic group, but they are differently dependent on π-donor properties of these groups. On the other hand, the cations of investigated metals are also π-donors, and therefore, this π-in-

(48) Irving, H.; Williams, R. J. P. _J. Chem. Soc._ **1953**, 3192.
(49) Jones, J. G.; Poole, J. B.; Tomkinson, J. C.; Williams, R. J. P. _J. Chem. Soc._ **1958**, 2001.

Table V. log K Values of Complexes between Metal Ion and Substituted Monocarboxylate Complexes Obtained at t = 25.0 ± 0.1 °C (18.0 ± 0.1 °C for CLAC Only) and I = 2 mol/L (NaClO$_4$)

metal ion	log K [method (ref)] CLAC	CNAC	PHAC	metal ion.	log K [method (ref)] CLAC	CNAC	PHAC
Co^{2+}	0.01 ± 0.01 [sp (12)] 0.38 ± 0.03 [pt (14)]	0.39 ± 0.02 [pt (33)]	0.62 ± 0.01 [pt (29)]	Zn^{2+}	0.95 ± 0.04 [pl (13)] 0.40 ± 0.01 [pt (14)]	0.50 ± 0.02 [pt (33)]	
av	0.19 ± 0.02	0.39 ± 0.02	0.62 ± 0.01	av	0.68 ± 0.03	0.50 ± 0.02	
Ni^{2+}	0.01 ± 0.01 [sp (12)] 0.20 ± 0.02 [pt (14)]	0.44 ± 0.02 [pt (33)]	0.65 ± 0.01 [pt (29)]	Cd^{2+}	0.84 ± 0.01 [pt (14)]	0.70 ± 0.02 [pt (33)]	1.15 ± 0.01 [pt (29)]
av	0.10 ± 0.02	0.44 ± 0.02	0.65 ± 0.01	Pb^{2+}	1.48 ± 0.04 [pl (13)] 1.51 ± 0.07 [pt (14)]	1.14 ± 0.02 [pt (33)]	
Cu^{2+}	1.26 ± 0.09 [sp (12)] 1.20 ± 0.03 [pl (13)]	0.93 ± 0.02 [pt (33)]		av	1.50 ± 0.06	1.14 ± 0.02	
av	1.23 ± 0.06	0.93 ± 0.01					

metal ion	log K [method (ref)] GLYCO	MAND	PIRU	metal ion	log K [method (ref)] GLYCO	MAND	PIRU
Co^{2+}	1.30 ± 0.02 [sp (12)] 1.48 ± 0.02 [pt (14)]	1.23 ± 0.01 [pt (36)]	0.61 ± 0.02 [pt (31)] 0.71 ± 0.04 [sp (31)]	Zn^{2+}	1.92 ± 0.04 [pl (13)] 1.72 ± 0.05 [pt (14)]	1.38 ± 0.01 [pt (36)]	0.74 ± 0.03 [pt (31)]
av	1.39 ± 0.02	1.23 ± 0.01	0.66 ± 0.03	av	1.82 ± 0.05	1.38 ± 0.01	0.74 ± 0.03
Ni^{2+}	1.62 ± 0.04 [sp (12)] 1.69 ± 0.02 [pt (14)]	1.33 ± 0.01 [pt (36)]	0.73 ± 0.02 [pt (31)] 0.82 ± 0.02 [sp (31)]	Cd^{2+}	1.41 ± 0.03 [pl (13)] 1.51 ± 0.01 [pt (14)]		0.70 ± 0.03 [pt (13)]
av	1.66 ± 0.03	1.33 ± 0.01	0.78 ± 0.02	av	1.46 ± 0.02		0.70 ± 0.03
Cu^{2+}	2.23 ± 0.04 [sp (12)] 2.40 ± 0.04 [pl (13)] 2.46 ± 0.04 [sp (25)]		1.38 ± 0.03 [pt (31)] 1.39 ± 0.03 [sp (31)]	Pt^{2+}	1.90 ± 0.04 [pl (12)] 1.83 ± 0.05 [pt (14)]		1.51 ± 0.02 [pt (31)]
av	2.36 ± 0.04		1.39 ± 0.03	av	1.87 ± 0.05		1.51 ± 0.02

metal ion	log K [method (ref)] LACT	3OHP	GLYCE	metal ion	log K [method (ref)] LACT	3OHP	GLYCE
Co^{2+}	1.28 ± 0.02 [sp (15)] 1.48 ± 0.02 [pt (26)]	0.49 ± 0.02 [sp (15)] 0.86 ± 0.02 [pt (26)]	1.18 ± 0.04 [sp (22)] 1.30 ± 0.04 [pt (22)]	Zn^{2+}	1.32 ± 0.04 [pl (10)] 1.67 ± 0.01 [pt (26)]	0.86 ± 0.10 [pt (15)] 0.86 ± 0.02 [pt (26)]	1.46 ± 0.02 [pt (30)]
av	1.38 ± 0.02	0.68 ± 0.02	1.24 ± 0.04	av	1.50 ± 0.03	0.86 ± 0.02	1.46 ± 0.02
Ni^{2+}	1.57 ± 0.02 [sp (15)] 1.71 ± 0.02 [pt (26)]	0.78 ± 0.03 [sp (15)] 0.96 ± 0.02 [pt (26)]	1.32 ± 0.04 [sp (22)] 1.46 ± 0.04 [pt (22)]	Cd^{2+}	1.48 ± 0.03 [pl (9)] 1.29 ± 0.02 [pt (26)]	1.15 ± 0.05 [pl (17)] 1.26 ± 0.04 [pt (26)]	1.60 ± 0.04 [pl (11)] 1.25 ± 0.03 [pt (30)]
av	1.64 ± 0.02	0.87 ± 0.03	1.39 ± 0.04	av	1.39 ± 0.03	1.22 ± 0.05	1.43 ± 0.04
Cu^{2+}	2.52 ± 0.04 [pt (9)] 2.54 ± 0.03 [pl (10)] 2.63 ± 0.03 [sp (15)] 2.66 ± 0.02 [pt (26)]	1.76 ± 0.03 [sp (15)] 1.83 ± 0.02 [pt (26)]	2.27 ± 0.04 [sp (22)] 2.18 ± 0.02 [pt (22)]	Pb^{2+}	1.88 ± 0.03 [pl (9)] 2.15 ± 0.04 [pl (10)] 2.16 ± 0.02 [pt (26)] 2.05 ± 0.02 [pl (32)] 2.05 ± 0.02 [vl (35)]	2.13 ± 0.04 [pl (17)] 2.10 ± 0.02 [pt (26)]	2.53 ± 0.04 [pl (11)] 2.10 ± 0.03 [pt (30)]
av	2.59 ± 0.03	1.80 ± 0.03	2.23 ± 0.03	av	2.06 ± 0.03	2.12 ± 0.03	2.32 ± 0.04

metal ion	log K [method (ref)] 2OHB	3OHB	4OHB	metal ion	log K [method (ref)] 2OHB	3OHB	4OHB
Co^{2+}	1.43 ± 0.03 1.49 ± 0.03	0.75 ± 0.06 0.91 ± 0.02	0.48 ± 0.03 [sp (20)] 0.45 ± 0.01 [pt (27)]	Zn^{2+}	1.72 ± 0.01	0.99 ± 0.01	0.96 ± 0.01 [pt (16)]
av	1.46 ± 0.03	0.83 ± 0.04	0.47 ± 0.02	Cd^{2+}	1.23 ± 0.07 1.29 ± 0.01	1.11 ± 0.02 1.28 ± 0.01	1.45 ± 0.03 [pl (17)] 1.33 ± 0.01 [pt (27)]
Ni^{2+}	1.72 ± 0.03 1.72 ± 0.03	1.00 ± 0.08 1.00 ± 0.01	0.52 ± 0.08 [sp (20)] 0.63 ± 0.01 [pt (27)]	av	1.26 ± 0.04	1.20 ± 0.02	1.39 ± 0.02
av	1.72 ± 0.03	1.00 ± 0.05	0.58 ± 0.05	Pb^{2+}	2.10 ± 0.05 2.10 ± 0.05 [pl (18)] 2.16 ± 0.05	2.17 ± 0.05 2.09 ± 0.01	2.28 ± 0.05 [pl (17)] 2.08 ± 0.02 [pt (27)]
Cu^{2+}	2.67 ± 0.02 2.63 ± 0.02 2.68 ± 0.06	1.83 ± 0.02 1.86 ± 0.02 1.93 ± 0.05	1.77 ± 0.03 [sp (19)] 1.80 ± 0.03 [pt (20)] 1.72 ± 0.04 [pl (24)]	av	2.12 ± 0.05	2.13 ± 0.03	2.18 ± 0.04
av	2.66 ± 0.03	1.87 ± 0.03	1.76 ± 0.03				

teraction destabilizes the metal ion–ligand interaction in comparison with the proton–ligand interaction resulting in nonunity slopes for pK(HL) vs log K(ML) relationships.

Table V summarizes the monoligand stability constants of substituted monocarboxylate complexes.

In Table VI the effect of the substituent in the monocarboxylate ligand on the stability of monoligand complexes is calculated and expressed as

$$\Delta \log K(\mathrm{ML}) = \log K(\mathrm{ML})_{\mathrm{exp}} - \log K(\mathrm{ML})_{\mathrm{calc}} \qquad (11)$$

where log K(ML)$_{\mathrm{exp}}$ is the experimentally obtained value while log K(ML)$_{\mathrm{calc}}$ is the value obtained from the straight line (Figure 1) by using coefficients from Table IV and pK values of the corresponding acid obtained in this laboratory (Table II). Δ log K(ML), therefore, represents the contribution of the substituent on the monoligand stability after the effect of basicity is extracted.

When the effect of substituents on the acetate ligand was analyzed, no additional contribution to the monoligand stability was determined with CN as substituent. This substituent changes the basicity of acetate ion (pK values 4.74 and 2.48 for acetic and cyanoacetic acids, respectively), but the CNAC ligand in complexation with metal ions behaves in accordance with the changed basicity. The same is true for phenyl as a substituent on the acetate ligand, only in this case the change in basicity is much smaller (pK(HL) of phenylacetic acid is 4.34 compared with 4.74 for acetic acid). The behavior of the CLAC ligand is similar, with some tendency toward an additional chelating stabilization effect found only with Cu^{2+} and Pb^{2+} ions (0.18 and 0.32 log K unit).

Table VI. Substituent Contribution to the Stability of Monoligand Monocarboxylate Complexes Expressed in log K Units

metal ion	Δ log K(ML)					
	CNAC	CLAC	PHAC	MAND	GLYCO	PYRU
Co^{2+}	0.04	0.01	0.01	0.76	0.86	0.34
Ni^{2+}	0.04	0.02	-0.04	0.80	1.06	0.32
Zn^{2+}	0.00	0.14		0.71	1.07	0.29
Cd^{2+}	0.03	0.12			0.44	0.09
Cu^{2+}	-0.04	0.18			0.89	0.50
Pb^{2+}	0.05	0.32			0.21	0.51

metal ion	Δ log K(ML)					
	LACT	3OHP	GLYCE	2OHB	3OHB	4OHB
Co^{2+}	0.85	0.04	0.74	0.93	0.20	-0.21
Ni^{2+}	1.03	0.14	0.82	1.11	0.28	-0.20
Zn^{2+}	0.74	-0.05	0.75	0.96	0.08	-0.01
Cd^{2+}	0.36	-0.01	0.47	0.23	-0.02	0.08
Cu^{2+}	1.10	0.02	0.85	1.18	0.10	-0.13
Pb^{2+}	0.38	0.11	0.76	0.45	0.14	0.05

OH as a substituent on the acetate ligand has a pronounced stabilizing effect over the ligand basicity (from 0.70 to 1.07 log K units) due to the stable five-membered chelate ring coordination, which was confirmed by an IR study of glycolate complexes in aqueous solutions.[50] Cd^{2+} and Pb^{2+} ions have a smaller tendency toward chelate stabilization than other investigated ions (only 0.44 and 0.21 log K unit for Cd^{2+} and Pb^{2+} ions, respectively).

Substituents on the propanoate ligand in the 2-position contribute also to additional chelate stabilization. The oxygen atom in the PYRU ligand additionally stabilizes the complex by 0.3–0.5 log K unit, while the OH group in the LACT ligand stabilizes the complex by for 0.7–1.1 log K units. In both systems the Cd^{2+} ion again shows the least pronounced tendency to form a five-membered chelate ring (0.09 and 0.36 log K unit for PYRU and LACT complexes, respectively). The Pb^{2+} ion in LACT complexes has the same lower chelate stabilization as the Cd^{2+} ion, but in PYRU complexes its chelatation is more pronounced (0.51 log K unit) possibly due to its large ionic radius, which enables it to coordinate with both OH groups. An OH group in the 3-position on the PROP ligand does not have any additional stabilizing effect, and 3OHP behaves in accordance to its basicity. This is quite understandable because a six-membered chelate ring should be formed, which is obviously not favorable in these systems.

An OH group as substituent in the BUTY ligand has a pronounced chelating stabilization only in the 2-position (about 1 log K unit), while in the 3- and 4-positions no stabilization effect was

registered. Again the Cd^{2+} and Pb^{2+} ions show the least pronounced chelatation (0.23 and 0.45 log K unit, respectively), but the Co^{2+} and Ni^{2+} ions show a slight tendency for additional stabilization over basicity with the 3OHB ligand of 0.2 log K unit, and a destabilization of the same amount with the 4OHB ligand below that expected from basicity relationship.

To illustrate how this analysis can be useful in predicting the stability of some other substituted monoligand monocarboxylate complexes, let us try to predict, for example, the stability of methoxyacetate and ethoxyacetate complexes of Co^{2+} and Ni^{2+}. Methoxyacetates should behave like mandelate complexes having almost the same pK(HL) value (3.31) and having the possibility for additional chelate coordination through the oxygen atom in the methoxy group. Ethoxyacetate (pK(HL) = 3.51) will have a less pronounced chelating effect due to the induced attraction of electrons in the ethoxy group. Therefore, the approximate log K(ML) values could be obtained by taking the basicity contribution (using coefficients in Table IV for Co^{2+} and Ni^{2+}) and corresponding pK values for methoxy- and ethoxyacetic acids and adding about 0.76 and 0.80 log K unit (from Table VI) for cobalt and nickel methoxyacetates, respectively, and 0.56 and 0.60 log K unit for cobalt and nickel ethoxyacetates, respectively. The obtained log K(ML) values are 1.22 and 1.33 for cobalt and nickel methoxyacetates, which agree well with the values 1.16 and 1.29 obtained experimentally under identical experimental conditions. The calculated values for cobalt and nickel ethoxyacetates are 1.02 and 1.13, which also agree well with the experimental values of 1.05 and 1.08.[51] In conclusion, it can be said that the performed analyses show the behavior of the investigated class of weak monocarboxylate complexes, comparing the effect of metal ion and ligand on the solution stability. The factors influencing this stability are quantitatively determined. In principle, the same analysis can be performed with higher complex types, but the reliability of the data is poorer because the experimental and data evaluation errors accumulate in higher cumulative stability constants. Such an analysis can be used as a model system for any weak coordinative interaction, and the stability of many new systems can be easily predicted by knowing the general trends.

(50) Larsson, L. *Acta Chem. Scand.* **1965**, *19*, 783.

(51) Savić, J.; Savić, M. *Bull. Soc. Chem. Technol. (Sarajevo)* **1974**, *21/22*, 17.

Notes

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Synthesis of New Carboxylate- and Phosphinate-Bridged Ruthenium(I) Dimers

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The carboxylate-bridged dimers of Ru(I) and Os(I) form an extensive class of derivatives with the general formula [M(μ-O$_2$CR)(CO)$_2$L]$_2$ (R = alkyl, fluoroalkyl, or aromatic; L = tertiary phosphine,[1] acetonitrile,[1] pyrazole,[2] carbon monoxide,[3] carboxylic

acid,[4,5] or pyridine[6]). Recent interest in these complexes stems in part from the discovery that they are catalyst precursors for the hydroformylation of olefins and the addition of carboxylic acids to alkynes.[7,8] Although a wealth of structural data is available for these complexes,[3,6,9,10] reports concerning their stoichiometric

(1) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G.; Gamlen, G. *J. Chem. Soc. A* **1969**, 2761.

(2) Neumann, F.; Süss-Fink, G. *J. Organomet. Chem.* **1989**, *367*, 175.
(3) Spohn, M.; Vogt, T.; Strähle, J. *Z. Naturforsch., B* **1986**, *41B*, 1373.
(4) Rotem, M.; Shvo, Y.; Goldberg, I.; Shmueli, U. *Organometallics* **1984**, *3*, 1758.
(5) Rotem, M.; Goldberg, I.; Shmueli, U.; Shvo, Y. *J. Organomet. Chem.* **1986**, *314*, 185.
(6) Bullitt, J. G.; Cotton, F. A. *Inorg. Chim. Acta* **1971**, *5*, 406.
(7) Jenck, J.; Kalck, P.; Pinelli, E.; Siani, M.; Thorez, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1428.
(8) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689.
(9) Schumann, H.; Opitz, J.; Pickardt, J. *J. Organomet. Chem.* **1977**, *128*, 253.