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Equilibrium Studies on the Complexation of Aluminum(III) and Vanadium(III) by Fluoride in Molten KSCN

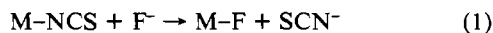
K. Jarring and B. Holmberg*

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The stepwise formation of fluoride complexes of Al(III) and V(III) in molten KSCN has been investigated at 185 °C. Fluoride activities were measured in systems (K⁺, Al³⁺)-(SCN⁻, F⁻) and (K⁺, V³⁺)-(SCN⁻, F⁻) by a recently developed potentiometric technique utilizing a fluoride-selective membrane electrode. Average ligand numbers from 0 to 4.3 and from 0 to 5.0 were obtained for the aluminum(III) and vanadium(III) systems, respectively. Higher ligand numbers were unattainable due to precipitation of K₃AlF₆ and K₃VF₆. Stability constants for five consecutive steps have been determined for both acceptor ions. A specific interaction parameter Δ*A*_{*j*} for each step of ligand exchange of thiocyanate for fluoride is determined. Average values, Δ*A* = -63.5 kJ·mol⁻¹ for Al³⁺ and Δ*A* = -40.4 kJ·mol⁻¹ for V³⁺, are obtained for the four first steps of complexation. The increase in total interaction energy for the fifth step is ascribed to increasing repulsion in the coordination sphere of the central ion as the number of fluoride ions increase or, alternatively for the Al³⁺ system, to a coordination change. Although the Coulomb hard-sphere interaction is considered to be dominating, it is found that a covalent contribution to the total interaction energy has to be taken into account in order to explain the stability sequence Cr³⁺ < V³⁺ < Al³⁺.

Introduction

This paper is part of a series of studies of polyvalent metal ion-fluoride complexation¹⁻³ aiming at a correlation of the influence of structural parameters, charge, and covalent interaction with the thermodynamics of the complexation process in ionic melts. A suitable measure of the energy change accompanying the ligand exchange



is provided by the quasi-lattice total interaction energy parameter Δ*A*_{*j*}.⁴ In previous papers it was concluded that the formation of fluoride complexes proceeds in a stepwise manner and that the total interaction energy of the ligand exchange is almost equal for each step *j*. It was proposed that the main part of the interaction energy change is due to Coulomb effects on replacement of the thiocyanate ion for the harder fluoride ion in the coordination sphere of hard acceptor ions like Co²⁺, Cr³⁺, VO²⁺, and UO₂²⁺. In the present paper the fluoride complexation of two more hard acceptor ions, Al³⁺ and V³⁺, have been investigated.

From studies in various melts⁵⁻⁹ as well as from work in aqueous solution¹⁰⁻¹² the ability of Al³⁺ to form very strong fluoride complexes is well documented. Unfortunately no investigations on aluminum species in molten thiocyanates have been published, so important information on the coordination and reactions of aluminum is not available.

The reactions of a series of vanadium compounds in different oxidation states in thiocyanate melts have been thoroughly investigated.¹³ It was concluded that +III and +IV are the stable oxidation states although melts containing vanadium(III) should be kept under vacuum or under inert gas atmosphere to prevent oxidation to vanadium(IV). From electronic absorption spectra an octahedral arrangement of thiocyanate ions, coordinated through the nitrogen end, was inferred. Fluoride complexes of V³⁺ do not seem to have been studied, neither in aqueous solution nor in melts of any kind.

Fluoride activities were measured by the same potentiometric

technique as in previous studies, utilizing a modified fluoride-selective membrane electrode.^{1-3,14}

Experimental Section

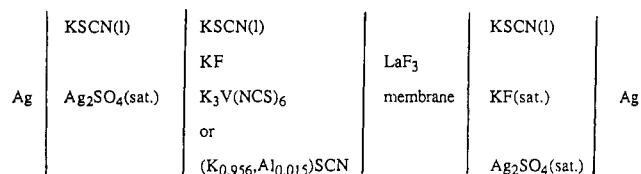
Chemicals. KSCN and KF were treated prior to use as described previously.^{1,14} K₃V(NCS)₆ was prepared by mixing VCl₃ and KSCN in a molar ratio of 1:6 in acetone. The mixture was stirred thoroughly, the precipitated KCl was filtered off, and the resulting solution was evaporated to dryness. The obtained yellow-brown salt was ground and dried, first under vacuum below 40 °C for several hours and then at 120 °C overnight. For analysis the salt was dissolved in an aqueous EDTA solution and back-titration was performed with a solution of Pb(NO₃)₂. The vanadium content found was 10.1% compared to the calculated value 9.9% for K₃V(NCS)₆.

All our efforts to prepare a stoichiometrically well-defined, pure potassium-aluminum-thiocyanate salt were unsuccessful. A solid mixture (K_{*x*}, Al_{*y*})SCN was therefore prepared in the following manner: Aqueous solutions of KAl(SO₄)₂·12H₂O and Ba(SCN)₂·2H₂O in a molar ratio of 1:2 were mixed, and the precipitated BaSO₄ was removed by filtration. A large excess of KSCN was added, and the water was removed by the action of vacuum for several days until no further weight loss could be detected. All work with preparation and drying of the (K_{*x*}, Al_{*y*})SCN mixture was performed at room temperature since decomposition occurred at temperatures as low as 50 °C. The same method of analysis used for the vanadium salt was employed to get the total aluminum concentration of the (K_{*x*}, Al_{*y*})SCN mixture. A double check of the composition was obtained by analyzing for the thiocyanate content by potentiometric titration with a silver(I) solution. The composition of the preparation used was (K_{0.956}, Al_{0.015})SCN. The possible presence of hydroxide species was checked by FTIR spectroscopy, revealing a complete absence of bands that might be ascribed to the hypothetical O-H stretching in the range 3000-4000 cm⁻¹.

VCl₃, K₃V(NCS)₆, (K_{0.956}, Al_{0.015})SCN, and chemicals containing fluoride were weighted and handled under dry N₂ atmosphere in a glovebox.

Emf Measurements. All potentiometric measurements were carried out under a flow of dry nitrogen in order to keep the test melts as dry as possible and to avoid oxidation of vanadium(III).

The treatment and design of the fluoride-selective membrane electrode used to measure fluoride activities were the same as in previous studies.^{1,14} The cell can be described as



Further details on furnaces, temperature control, cell construction, and measurements have been described elsewhere.^{1,15-17}

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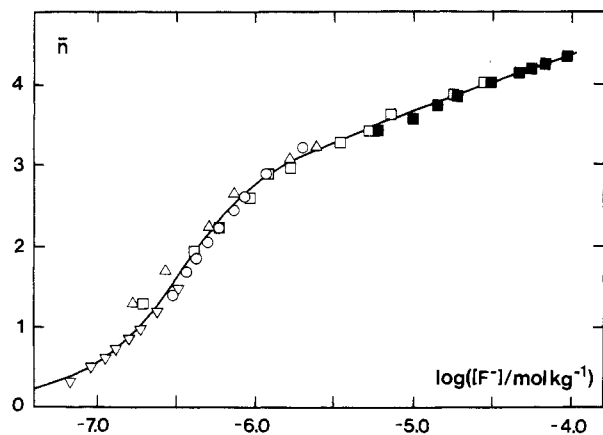


Figure 1. Typical experimental results from emf measurements of the fluoride activity in KSCN–KF melts containing Al^{3+} at 185 °C. Experimentally determined \bar{n} 's from different series are displayed. The marker symbols represent compositions in the entire composition ranges described in the Experimental Section. The full-drawn curve is constructed by use of the stability constants β_j in Table I.

The fluoride content of the test melts was varied by additions of KF or solidified stock melts of KF + KSCN. Aluminum(III) was added as $(\text{K}_{0.956}\text{Al}_{0.013})\text{SCN}$ and vanadium(III) as $\text{K}_3\text{V}(\text{NCS})_6$. Stable emf readings (± 0.1 mV) could be obtained within 30 min after the melt composition had been changed.

The ranges of total concentrations covered in the Al^{3+} system were $3.6 \times 10^{-4} < C_{\text{Al}}/(\text{mol}\cdot\text{kg}^{-1}) < 3.2 \times 10^{-3}$ and $1.0 \times 10^{-3} < C_{\text{F}}/(\text{mol}\cdot\text{kg}^{-1}) < 3.9 \times 10^{-3}$ and the measured free fluoride concentrations were in the range $5.1 \times 10^{-8} < [\text{F}^-]/(\text{mol}\cdot\text{kg}^{-1}) < 1.0 \times 10^{-4}$. Corresponding figures for the V^{3+} system were $2.4 \times 10^{-4} < C_{\text{V}}/(\text{mol}\cdot\text{kg}^{-1}) < 4.5 \times 10^{-3}$, $1.6 \times 10^{-3} < C_{\text{F}}/(\text{mol}\cdot\text{kg}^{-1}) < 1.4 \times 10^{-2}$, and $1.1 \times 10^{-5} < [\text{F}^-]/(\text{mol}\cdot\text{kg}^{-1}) < 7.8 \times 10^{-3}$.

The total time for a run, calibration of the electrode, and the complex formation study was 1 day. During this time a maximum of data points were collected as described recently.¹

Results and Discussion

The linear relation between the emf, E , and $\log [\text{F}^-]$

$$E = E_0 - k \log ([\text{F}^-]/(\text{mol}\cdot\text{kg}^{-1})) \quad (2)$$

has been shown to hold for the fluoride electrode cell in molten KSCN in the concentration range $3 \times 10^{-4} \leq C_{\text{F}}/(\text{mol}\cdot\text{kg}^{-1}) \leq 5 \times 10^{-1}$.¹⁴

The experimental emf data were used to derive $[\text{F}^-]$ from eq 2, and average ligand numbers, \bar{n} , were thus obtained from

$$\bar{n} = (C_{\text{F}} - [\text{F}^-])/C_{\text{M}} \quad (3)$$

where C_{M} is the total concentration of Al^{3+} (C_{Al}) or V^{3+} (C_{V}). Typical experimental data are displayed for the aluminum(III) system in Figure 1 and for the vanadium(III) system in Figure 2. The points were selected among the 105 and 83 measured ones for the Al^{3+} and V^{3+} systems, respectively. They are chosen to represent the normal spread and the extent of overlap in the runs performed. Different marker symbols define different experimental runs. As can be seen from Figures 1 and 2, \bar{n} is a function of $[\text{F}^-]$ only and it is not sensitive to variations in C_{M} . This means that no polynuclear complexes have to be taken into account in the data treatment.

Precipitation reactions limited the possibility to obtain higher average ligand numbers than ≈ 4.3 for Al^{3+} and ≈ 5.0 for V^{3+} . Since it was impossible to separate the solids from the melts without decomposition, chemical analysis of the compounds could not be performed. Instead, precipitation experiments utilizing the fluoride-selective electrode were set up. In order to safely assume the precipitation reactions to be dominating, test melts with far higher fluoride concentrations than in the complex formation studies were prepared. The emf was recorded before and

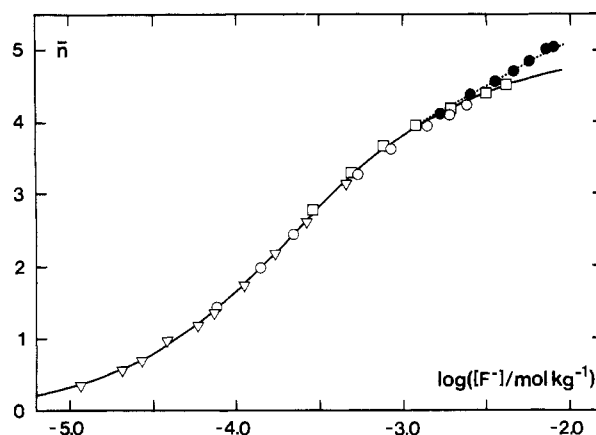


Figure 2. Typical experimental results from emf measurements of the fluoride activity in KSCN–KF melts containing V^{3+} at 185 °C. Experimentally determined \bar{n} 's from different series are displayed. The marker symbols represent compositions in the entire composition ranges described in the Experimental Section. The full-drawn curve is constructed by use of the stability constants β_j in Table I. A tentative value, $\beta_6 = 1.0 \times 10^{20} \text{ mol}^{-6}\cdot\text{kg}^6$, has been introduced to construct the dashed line.

Table I. Overall and Stepwise Stability Constants for AlF_j^{3-j} and VF_j^{3-j} in Molten KSCN at 185 °C^a

j	Al^{3+}		V^{3+}	
	$\beta_j/(\text{mol}^{-j}\cdot\text{kg}^j)$	$K_j/(\text{mol}^{-1}\cdot\text{kg})$	$\beta_j/(\text{mol}^{-j}\cdot\text{kg}^j)$	$K_j/(\text{mol}^{-1}\cdot\text{kg})$
1	$(6.3 \pm 1.6) \times 10^6$	6.3×10^6	$(3.6 \pm 0.2) \times 10^4$	3.6×10^4
2	$(1.1 \pm 0.4) \times 10^{13}$	1.8×10^6	$(3.8 \pm 0.2) \times 10^8$	1.0×10^4
3	$(5.0 \pm 0.8) \times 10^{19}$	4.4×10^6	$(1.4 \pm 0.1) \times 10^{12}$	3.8×10^3
4	$(8.4 \pm 1.2) \times 10^{24}$	1.7×10^5	$(3.4 \pm 0.2) \times 10^{15}$	2.4×10^3
5	$(6.2 \pm 1.6) \times 10^{28}$	7.4×10^3	$(1.1 \pm 0.1) \times 10^{18}$	3.3×10^2

^aThe error limits define a 95% confidence interval.

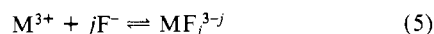
after additions of metal ions. It was thus possible to obtain the number of fluoride ions coordinated in the precipitates. The number found was in both cases very close to 6, so it is concluded that the solid compounds formed are K_3AlF_6 and K_3VF_6 . Conditional solubility constants, K'_s , for these compounds can be expressed as

$$K'_s = [\text{M}^{3+}][\text{F}^-]^6 \quad (4)$$

K'_s was estimated at 185 °C to $(4 \pm 1) \times 10^{-37} \text{ mol}^7\cdot\text{kg}^{-7}$ for K_3AlF_6 and to $(2.5 \pm 0.5) \times 10^{-24} \text{ mol}^7\cdot\text{kg}^{-7}$ for K_3VF_6 . These estimates are based on knowledge of the association constants from Table I and visual observations of the onset of precipitation of the fluoride compounds in the test melts.

An instability and rapid change in the measured emf were observed when data with $[\text{F}^-] < 10^{-7.2} \text{ mol}\cdot\text{kg}^{-1}$ were recorded in the aluminum(III) system (Figure 1), and the run had to be terminated. On recalibration of the LaF_3 membranes in pure KSCN–KF melts, it was found that the slope of the electrodes had decreased to 40–80% of their original value. The same membranes could, however, be used in fluoride activity measurements in molten $(\text{K},\text{Na})\text{NO}_3$ at 280 °C with a slope close to the theoretical.¹⁸ After this treatment they worked in KSCN melts again, with their original performance. ESCA analysis of the malfunctioning membranes showed a marked reduction of intensities in all parts of the spectrum, compared to those in the spectrum obtained from a fresh membrane surface. This was interpreted as a roughening of the membrane surface due to dissolution of some LaF_3 into the melt.

The formation of MF_j^{3-j} species can be described by a set of overall equilibria



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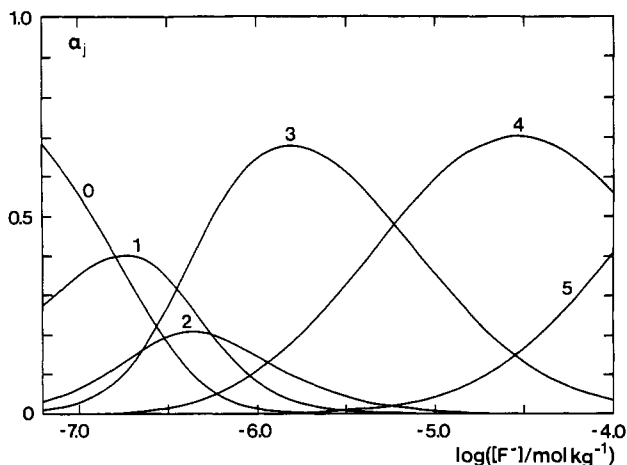


Figure 3. Fraction α_j of Al in different complexes AlF_j^{3-j} in molten KSCN-KF at 185 °C. j is indicated on the curves.

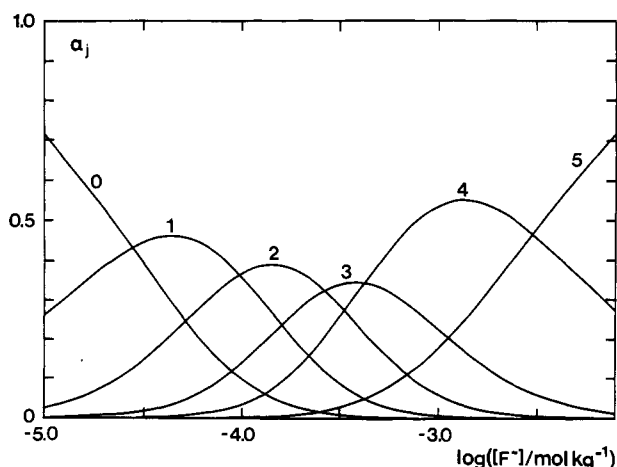


Figure 4. Fraction α_j of V in different complexes VF_j^{3-j} in molten KSCN-KF at 185 °C. j is indicated on the curves.

where coordinated SCN^- ions have been omitted for the sake of clarity. The cumulative and stepwise stability constants β_j and K_j are defined in the conventional way.¹ The stability constants were calculated by a recently described least-squares method, minimizing the sum $\sum (E_{\text{exptl}} - E_{\text{calcd}})^2$.¹ It is clear from Figures 1 and 2 that association constants for at least five consecutive steps can be determined in each system. The discrepancy at high fluoride concentrations in the vanadium(III) system is due to the low concentration of metal ion needed to avoid precipitation of K_3VF_6 . The error $|E_{\text{exptl}} - E_{\text{calcd}}|$ is actually as low as a few tenths of a millivolt. If an even better fit to experimental \bar{n} values is desired, a sixth complex has to be introduced. The measurements of this study do not allow us to calculate a statistically significant value of β_6 , but for comparison reasons a tentative value, $1.0 \times 10^{20} \text{ mol}^{-6} \cdot \text{kg}^6$, was used together with β_1 - β_5 of Table I to construct the dashed curve in Figure 2.

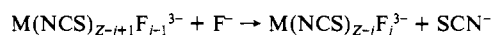
The fraction α_j of different species is defined as

$$\alpha_j = [\text{MF}_j^{3-j}] / C_M \quad (6)$$

Here α_0 is the fraction of metal ion coordinated to SCN^- only. Figures 3 and 4 show the species distribution for the aluminum(III) and vanadium(III) systems, respectively. In neither case is there a single dominating species at any free fluoride concentration. The relative stability of the third complex over those of the two first complexes in the aluminum(III) system has a marked influence on the species distribution, however.

The smoothness of the complex formation and distribution curve for vanadium(III) suggests that the fluoride complexation can be described by a simple ligand-exchange process (1) in every step. According to the quasi-lattice theory for complex formation in

Table II. Total Interaction Energies, ΔA_j , for the Ligand-Exchange Reaction



Where Z is the Quasi-Lattice Coordination Number^a

j	$-\Delta A_j / (\text{kJ} \cdot \text{mol}^{-1})$			
	Al^{3+}		$\text{V}^{3+}, Z = 6$	$\text{Cr}^{3+}, Z = 6$
	$Z = 4$	$Z = 6$		
1	63.2 ± 1.1	61.7 ± 1.1	42.0 ± 0.2	34.7 ± 1.0
2	62.2 ± 2.2	60.3 ± 2.2	40.6 ± 0.2	39.3 ± 0.9
3	68.7 ± 1.8	66.0 ± 1.8	39.2 ± 0.2	34.4 ± 1.7
4	60.0 ± 0.9	55.8 ± 0.9	39.6 ± 0.3	37.3 ± 1.9
5		46.3 ± 1.3	34.4 ± 0.3	
$-\Delta A$	63.5	61.0	40.4	36.4

^a The error limits define a 95% confidence interval. ΔA denotes an average value of the total interaction energy for the four first complexation steps. Data for Cr^{3+} are taken from ref 1.

reciprocal molten salt systems,⁴ the change in total acceptor-donor interaction energy ΔA_j for the j th step can be calculated as

$$\Delta A_j = RT \ln [(Z - j + 1)j^{-1}K_j^{-1}] \quad (7)$$

provided the complexation is strong, i.e. $\exp(-\Delta A_j/RT) \gg 1$. The stepwise association constants K_j are expressed in mole fraction units, and Z is the quasi-lattice coordination number. The octahedral arrangement of ligands around V^{3+} , in molten KSCN as well as in solid thiocyanate and fluoride compounds, yields $Z = 6$ for vanadium(III). No information on aluminum-thiocyanate coordination from molten salt studies nor from simple solid compounds seems to be available. Therefore, ΔA_j for the two most reasonable coordination geometries, tetrahedral ($Z = 4$) and octahedral ($Z = 6$) were computed. The main argument in favor of a tetrahedral configuration over an octahedral one is the small size of the aluminum ion,¹⁹ making it hard to accommodate six thiocyanate ions. On the other hand, aluminum certainly coordinates six fluorides in the precipitate K_3AlF_6 . Hence, if the tetrahedral arrangement is chosen as starting point, a coordination change must occur as the complexation proceeds. In this respect, the coordination chemistry of Al(III) in mixed KSCN-KF melts at this low temperature bears an obvious resemblance to the chemistry in pure alkali fluoride-aluminum fluoride molten mixtures in which tetrahedral and octahedral species are present in equilibrium.^{6,7}

The interaction energies of the Al^{3+} and V^{3+} systems together with the earlier investigated Cr^{3+} system are collected in Table II. The closeness of ΔA_1 - ΔA_4 in all three systems implies that the complexation over all four steps can be described by a single interaction energy, ΔA , for each system. The increase in interaction energy for the fifth step is probably due to an increase in electrostatic repulsion as the number of coordinated fluoride ions increases. A coordination change for aluminum(III) at this step should also have a pronounced effect on the calculated interaction energy. The configurational entropy change accompanying such a process is not predictable, so no value of ΔA_5 is given in Table II in this case. The obtained stability sequence $\text{Cr}^{3+} < \text{V}^{3+} < \text{Al}^{3+}$ for the ligand exchange (1) cannot be explained solely by a change in hard-sphere Coulomb interaction energy. A simple calculation based on point charges and interatomic distances from crystal structure data,²⁰⁻²⁵ of compounds having complex anions of the same kind as the complex species in the melt, gives the stability sequence $\text{V}^{3+} < \text{Cr}^{3+} < \text{Al}^{3+}$. A hard-sphere model is obviously not sufficient for prediction of the correct order between

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vanadium and chromium. A "soft" contribution to the interaction energy may be schematically introduced according to

$$\Delta A = \Delta A_{\text{Coulomb}} + \Delta A_{\text{soft}} \quad (8)$$

The softer the metal ion, the stronger its covalent interaction with thiocyanate, and thus an increasing *positive* contribution, ΔA_{soft} , to the total interaction energy would be the result. Hence, the effect of introducing ΔA_{soft} is to counteract the ligand exchange (1) to various extents for the acceptor ions considered here. Ahrlund²⁶ suggested that a softness parameter, basically the sum of ionization energy and hydration enthalpy, may be taken as a good measure of the softness character of acceptor ions. This approach was later elaborated by Marcus,²⁷ who demonstrated

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the applicability of the softness scale to molten salt mixtures. The softness character decreases in the orders $\text{Cr}^{3+} > \text{V}^{3+} \approx \text{Al}^{3+}$ and $\text{SCN}^- > \text{F}^-$. ΔA_{soft} is thus expected to increase in the order $\text{Cr}^{3+} > \text{V}^{3+} \approx \text{Al}^{3+}$, which may be the underlying reason for the interchange of chromium(III) and vanadium(III) in the observed stability sequence as compared to the one calculated from a hard-sphere model. The predictive power of the schematic eq 8 might be explored in a more quantitative aspect by correlating a larger amount of experimental thermodynamic data on complexation in melts with ionic charges, interatomic distances, and softness parameters.

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Supplementary Material Available: A listing of experimental emf data (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Metal Complexes of Nickel, Cobalt, and Iron Having Monomeric 15-Membered Lacunar Cyclidene Ligands, with a Representative Crystal Structure. Dioxygen Binding by the Cobalt Complexes

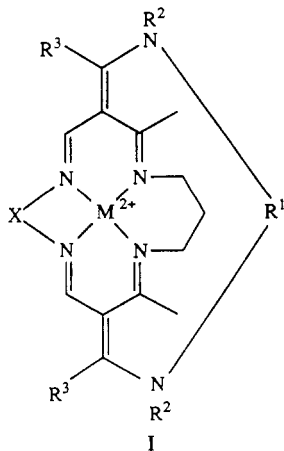
Rudolf Thomas, Carol M. Fendrick, Wang-Kan Lin, Mark W. Glogowski, Madhav Y. Chavan, Nathaniel W. Alcock,* and Daryle H. Busch*

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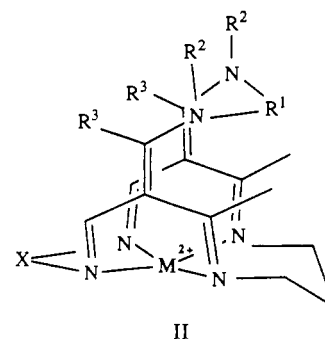
Lacunar nickel(II) complexes of 15-membered cyclidene ligands, having $(\text{CH}_2)_n$ ($n = 5-8, 12$) or *m*-xylylene bridging units, have been synthesized by a template process. The X-ray crystal structure of the derivative with $n = 6$, (2,3,10,11,13,19-hexamethyl-3,10,14,18,21,24-hexaazabicyclo[10.7.6]pentacos-1,11,13,18,20,24-hexaene- κ^4 N)nickel(II) hexafluorophosphate (Vb), $\text{C}_{25}\text{H}_{42}\text{N}_6\text{Ni}(\text{PF}_6)_2$, has been determined: triclinic, $P\bar{1}$, $a = 10.406$ (2) Å, $b = 14.044$ (4) Å, $c = 14.251$ (4) Å, $\alpha = 91.14$ (2)°, $\beta = 109.38$ (2)°, $\gamma = 111.11$ (2)°, $Z = 2$, and refined to $R = 0.096$ for 5095 $I > 3\sigma(I)$ data. The ligand salts have been prepared by demetalation of the nickel(II) complexes with HCl(g). Corresponding cobalt(II) complexes and an iron(II) complex have been prepared. The K_{O_2} values for the cobalt(II) complexes were obtained in acetonitrile/1.5 M *N*-methylimidazole.

Introduction

The development of model complexes for heme proteins that can provide insight into the factors important to enhancement of the ability to bind dioxygen presents a continuing challenge.¹⁻³ For example, the works of Collman⁴ and Baldwin⁵ have emphasized steric factors, while Traylor⁶ has examined electronic factors in the binding of small ligands to heme type units. The cyclidene complexes, which have general structure I, are of interest as totally



synthetic (nonporphyrin) models of heme proteins. The overall saddle shape of these complexes (structure II, $\text{X} = (\text{CH}_2)_3$)



provides a cavity within which small ligands can be bound, dioxygen in the cases of the cobalt(II) and iron(II) complexes. Previous reports have shown that these cobalt(II)⁷ and iron(II)^{8,9}

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