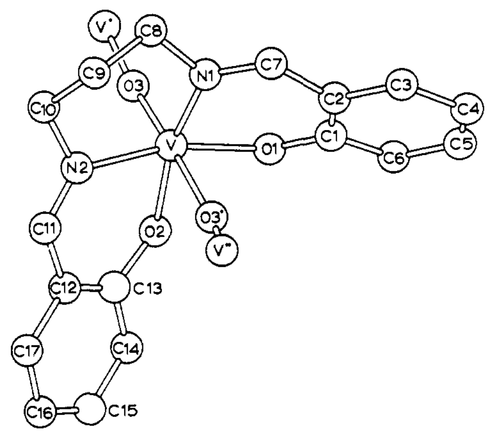

Figure 1. A view of the VO(salpn) molecule illustrating the atomic numbering. The atoms V′, O3′, and V″ are from neighboring molecules and show the polymeric nature of the compound. The pertinent angles are O3-V-O1, 104.0; O3-V-O2, 103.3; O3-V-N1, 94.0; O3-V-N2, 94.5; O3-V-O3′, 168.8; O1-V-O2, 86.3; O1-V-N1, 88.4; N1-V-N2, 91.6; N2-V-O2, 88.2; V-O3-V′, 158.2°. All angles are ±0.6°.

nitrogen *trans* to a vanadyl oxygen.[3] The V-O3 distance of 1.633 (9) Å is one of the longest vanadyl oxygen distances reported to date, the range being from 1.571 (10) to 1.62 (1) Å.[9] The longer V-O distance in VO(salpn) is consistent with the lower stretching frequency *vide infra* and the bridging character of the vanadyl oxygen atom.

The in-plane V-O bond distances (those normal to the vanadyl oxygen atom) are V-O1 of 1.943 (9) Å and 1.947 (9) Å, average 1.945 (9) Å, and are similar to those found in N,N′-ethylenebis(1-acetonylethylideniminato)oxovanadium(IV), VO(acen), where they average 1.950 (6) Å,[2] and are slightly shorter than the V-O (water molecules *cis* to the vanadyl oxygen) bonds, average 2.040 (5) Å, found in $[OV(H_2O)_4SO_4]H_2O$.[8] Similarly the V-N bonds in VO(salpn) (*cis* to the vanadyl group), V-N1 of 2.100 (13) and V-N2 of 2.124 (13) Å, average 2.112 (13) Å, are longer than in VO(acen),[2] average 2.053 (6) Å, but similar to the average of 2.08 (2) Å found in deoxophylloerythroetioporphyrinoxovanadium(IV), VO(por).[4] Therefore the V-ligand distances in VO(salpn) are similar to those found in other vanadyl derivatives, and the unusual characteristics of VO(salpn) must be related to other properties of the molecule.

The most striking difference between VO(salpn) and other vanadyl complexes involving chelating ligands is the more nearly planar nature of the molecule. The V atom is displaced by only 0.31 Å from the plane defined by the O1, O2, N1, and N2 atoms compared to 0.54–0.58 Å in other complexes.[10] The planar nature of the complex together with the interaction of the vanadyl oxygen atom with a second vanadium atom could account for the difference in color between VO(salpn) and other complexes.

A comparison of the infrared spectra of VO(salpn), the free ligand, and the copper complex of the ligand shows that $\nu(V{=}O)$ appears at 854 cm^{-1} as a very intense absorption. Since the $\nu(V{=}O)$ stretching mode of oxovanadium(IV) complexes generally is in the range 910–1010 cm^{-1}, the value of 854 cm^{-1} is the lowest $\nu(V{=}O)$ frequency reported to date. Ginsberg[11] has tentatively suggested that low $\nu(V{=}O)$ frequencies may be due to bridging vanadyl groups, although no structural data are available. We are currently investigating $VO(2,2'\text{-bipyridine})Cl_2$ and $VO(1,10\text{-phenanthroline})Cl_2$, which also have low $\nu(V{=}O)$ frequencies.[12] Since the low $\nu(V{=}O)$ frequency of 854 cm^{-1} is within the range (650–920 cm^{-1}) expected for bridging M-O-M bonds,[13] the presence of this band may prove to be an excellent diagnostic test for oxygen bridging in these systems.

Acknowledgment. We wish to thank the National Research Council of Canada for financial support.

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[9] The earlier V-O distances are summarized in ref 5.

[10] The values for some individual complexes have been summarized in ref 2.

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Evidence for a Three-Coordinate Complex of Nickel(II)

Sir:

We have obtained evidence for the formation of the very unusual three-coordinate $NiCl_3^-$ complex in liquid $CsAlCl_4$ at 400–750°.

Dilute solutions of Ni(II) in liquid $CsAlCl_4$ containing on the order of 10^{-3} *M* added CsCl were found to have an unusual absorption spectrum. Upon increasing the CsCl concentration this spectrum was progressively replaced by that of $NiCl_4^{2-}$. The equilibrium solubility of solid $CsNiCl_3$ in such melts was found to obey the relation [Ni(II), total] = a[CsCl] + k_1 at 400–480°, where a and k_1 are constants at a given temperature. Quantitative spectrophotometric measurements showed unambiguously that the concentration dependence of this expression was due entirely to changes in the concentration of $NiCl_4^{2-}$ while the concentration of the new species stayed constant. Therefore, the new species has the stoichiometry of $(NiCl_3)_n^{n-}$, apart from solvation, and the dissolution of $CsNiCl_3$ may be represented by the two heterogeneous equilibria

$$nCsNiCl_3(s) = (NiCl_3)_n^{n-}(soln) + nCs^+(soln) \qquad (1)$$

$$CsNiCl_3(s) + Cl^-(soln) = NiCl_4^{2-}(soln) + Cs^+(soln) \qquad (2)$$

Because $[Cs^+]$ was essentially constant in these systems and because $[Cl^-]$ due to added CsCl was great enough to permit neglect of the equilibrium $2AlCl_4^- = Al_2Cl_7^- + Cl^-$, it follows that $(1/n)[(NiCl_3)_n^{n-}] = k_1$ and $[NiCl_4^{2-}]/[Cl^-] = a/(1 - a) = k_2$, where $[Cl^-] = [CsCl] - [NiCl_4^{2-}]$. Experimentally, log k_1 and log k_2 were found to be linear functions of $1/T$.

The homogeneous equilibrium between $NiCl_4^{2-}$(soln) and $(NiCl_3)_n^{n-}$(soln) was studied spectrophotometrically over a wide Cl^- concentration range at 500–750° for nickel concentration below saturation with respect to solid phases. Absorbance values at 14 wavelengths accurately fitted the relationship $k_3 = [NiCl_3^-][Cl^-]/[NiCl_4^{2-}]$, where k_3 is a constant at a fixed temperature. Therefore, the homogeneous equilibrium is accurately represented by

$$NiCl_4^{2-}(soln) = NiCl_3^-(soln) + Cl^-(soln) \qquad (3)$$

apart from solvation of $NiCl_3^-$, *i.e.*, n is unity. This fitting was done by digital computer which simultaneously generated k_3 values and the spectra of the component species. The latter are shown in Figure 1. Band maxima for $NiCl_3^-$ are at 13,100 and 17,700 cm^{-1}. The quantity log k_3 was a linear function of $1/T$ over the range 500–750°.

From the temperature dependence of k_1, k_2, and k_3 it was found that $\Delta H_1^\circ \cong 25.8$ kcal, $\Delta S_1^\circ \cong 23.5$ cal/deg, $\Delta H_2^\circ = 13.1$ kcal, $\Delta S_2^\circ \cong 14.6$ cal/deg, $\Delta H_3^\circ = (13.3 \pm 0.2)$ kcal, and $\Delta S_3^\circ = (9.8 \pm 0.1)$ cal/deg. Since eq 1, 2, and 3 are interdependent, $\Delta H_3^\circ - \Delta H_2^\circ + \Delta H_1^\circ$ and $\Delta S_3^\circ - \Delta S_2^\circ + \Delta S_1^\circ$ should equal zero, which they do to within experimental uncertainty.

The spectrum of $NiCl_3^-$ differs markedly from the spectra for approximately octahedral[1-3] and approximately tetrahedral[3,4] chloronickel(II) entities in crystals, molten salts, and other solutions. In this respect the absence of a spin-allowed band between 5000 and 13,000 cm^{-1} is noteworthy. This result rules against the monosolvated species $NiCl_3AlCl_4^{2-}$, which, in analogy to $NiCl_3ZnCl_4^{3-}$, would be expected to consist of ($NiCl_4$) and ($AlCl_4$) tetrahedra that share a corner.[4] Øye and Gruen[5] have given preliminary evidence for precisely this entity in liquid $KAlCl_4$.

The unusual spectrum of $NiCl_3^-$ is satisfactorily rationalized in terms of D_{3h} point group geometry. Computer calculations of the energy levels for this geometry utilized the tensor operator equations described by Wybourne[6] with B_0^2 and B_0^4 as potential parameters. Values of the two electronic repulsion parameters and the spin-orbit coupling constant were the same as those used by DeKock and Gruen[7] for gaseous $NiCl_2$. (The latter three parameters have about the same values for all chloronickel(II) entities.) Best fits between calculated and observed transition energies were achieved with $B_0^2/B_0^4 = -8/3$ and 5/3. In the electrostatic point-charge model the former corresponds to a weak axial perturbation and the latter to a strong axial perturbation, *i.e.*, $NiCl_3(AlCl_4)_2^{3-}$. The latter entity cannot be reconciled with the large, positive value as ΔS_3° unless the reaction is accompanied by a large structural change in the solvent. But the available evidence indicates that liquid alkali metal tetrachloroaluminates containing an excess of alkali metal chloride do not have elaborate or rigid interionic structures.[5,8-12] For this reason we discard the five-coordinate entity $NiCl_3(AlCl_4)_2^{3-}$ as very improbable and conclude that $NiCl_3^-$ is not complexed to solvent ions. It is, of course, weakly perturbed by the coulomb field due to solvent ions above and below the molecular plane in a way that is analogous to the perturbation of nitrate ions by surrounding ions in a molten alkali metal nitrate.

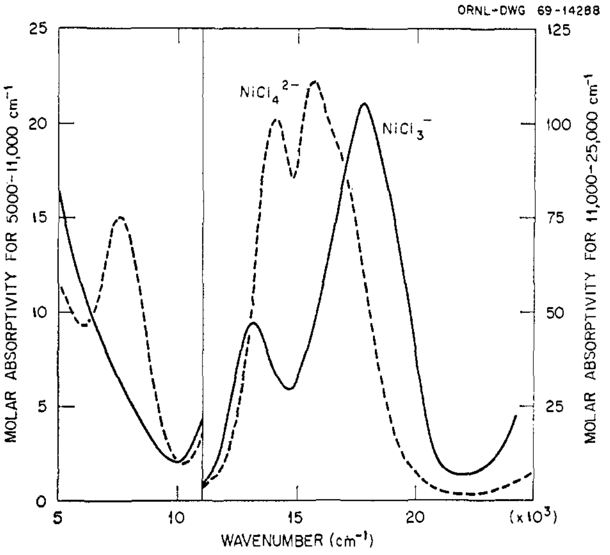

Figure 1. Spectra of $NiCl_4^{2-}$ and $NiCl_3^-$ in molten $CsAlCl_4$ containing small amounts of added CsCl at 600°. Calculated from spectra of mixtures using exprimental k_3 value.

Final values of B_0^2 and B_0^4 for $NiCl_3^-$ were 13,300 and −3900 cm^{-1}, respectively. These compare[7] with −12,600 and −4200 cm^{-1}, respectively, for gaseous $NiCl_2$ and, hence, have a reasonable magnitude.

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Photodimerization of Norbornadiene Using Chromium Hexacarbonyl

Sir:

During the course of our investigations into the mechanistic details of metal carbonyl assisted photodimerization of norbornadiene,[1] we have extended the number of useful metal carbonyls and identified one of the intermediates in the reaction.

Norbornadiene was first dimerized photochemically by Pettit[2] using $Fe(CO)_5$, and the reaction was further characterized by Lemal.[3] Other workers have shown that norbornadiene can be dimerized thermally using $Ni(CO)_4$,[4] $((C_6H_5)_3P)_2Co_2(CO)_6$,[5] $Fe(NO)_2(CO)_2$,[6] $Co(CO)_3NO$,[6] and $Fe_2(CO)_9$.[7] Schrauzer has added other olefins to norbornadiene thermally and suggested

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