lamp filtered to provide radiation near 500 nm so that again only R was excited. The phosphorescence decays of donor and acceptor could be measured separately by monitoring different wavelengths (Figure 1). They also have different decay lifetimes, 33 μsec for R and 380 μsec for C at $-65°$. From oscilloscope traces of the decay measured at 751 nm (at the phosphorescence maximum of R) a Stern–Volmer plot was obtained (Figure 2). The slope of this plot of reciprocal lifetime, $1/\tau_R$, against concentration of C gives directly the value of k_{et} as $6.6 \times 10^5\ M^{-1}\ sec^{-1}$. The emission at 840 nm (where only C emits) shows an initial increase in intensity with time followed by a longer decay. That increase represents the lifetime of the donor (R) excited state and the value obtained agrees with that found directly from the decay of R phosphorescence. The decay lifetime of C phosphorescence is somewhat smaller (250 μsec) in the presence of 0.05 M R than in its absence; thus, there is some back-energy-transfer from C to R or quenching by R. From these data, the reverse energy transfer rate constant, k_{et}', is calculated to be $2.7 \times 10^4\ sec^{-1}$. This is consistent with the fact that the reverse transfer must be endothermic by 870 cm^{-1}.

The lifetime of the phosphorescing state of R at $-65°$ is 33 μsec in the absence of C. This value of $\tau_R{}^0$ can be used to find k_{et} from the steady-state Stern–Volmer constants. Using the average value of 22.3 M^{-1}, we find $6.9 \times 10^5\ M^{-1}$ for k_{et}, in good agreement with that found directly from lifetime measurements.

These results on quenching, sensitization, and lifetime establish unequivocally that the excited states of the donor and acceptor molecules involved are ^2E_g.[5] We cannot draw quantitative conclusions yet about the relative importance of energy transfer and of quenching reactions. It is apparent, however, that energy transfer from R to C is of major importance. With regard to the detailed mechanism, we also cannot distinguish the case that the phosphorescing state of R is directly involved in the transfer or that some thermally populated state is the immediate precursor to energy transfer. Our studies of the temperature dependence of k_{et}, to be reported in detail later, show that the lowest quartet state of R, about 16,000 cm^{-1} above the ground state, lies too high in energy to be involved in the transfer. Similarly, the $^4T_{2g}$ state of C cannot be involved. Energy transfer does not occur at temperatures below $-130°$, where the solvent becomes a rigid glass. This result, together with the magnitude of k_{et} itself, shows that energy transfer is a collisional process with a rate close to diffusion controlled ($k_{diff} \approx 4 \times 10^6\ M^{-1}\ sec^{-1}$ for our solvent estimated from viscosity measurements) at $-65°$. Energy transfer can not be detected at room temperature because the lifetime of the ^2E_g state of the donor decreases with increasing temperature faster than k_{et} increases and because of the importance of back-energy-transfer.

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An Unusual Complex Containing Bridging Vanadyl Groups. The Crystal Structure of N,N′-Propylenebis(salicylaldiminato)oxovanadium(IV)

Sir:

The yellow-orange color of the compound N,N′-propylenebis(salicylaldiminato)oxovanadium,[1] henceforth VO(salpn) with the formula $[OC_6H_4CH{=}NCH_2\text{-}CH_2CH_2N{=}CHC_6H_4O]VO$, appears to be a striking deviation from most oxovanadium complexes which tend to be blue or blue-green.[2-5] Our preparative, structural, and spectroscopic studies of this compound have indeed revealed an unusual interaction in which the vanadyl oxygen acts as a ligand in the solid state and possibly in solution.

The compound can be prepared as reported[1] or in dimethyl sulfoxide or pyridine. In all cases sparingly soluble, yellow-orange needles are formed. The crystals are orthorhombic with cell dimensions of a = 7.538 (2), b = 11.874 (4), and c = 17.235 (5) Å. The space group is $P2_12_12_1$ and, with four molecules per unit cell, the calculated density is 1.495 g/cm^3 compared with the value 1.474 g/cm^3 measured by flotation.[6] Three-dimensional intensity data were measured using the stationary crystal–stationary counter method with Cu Kα radiation and an automatic diffractometer. All the hkl reflections with $2\theta \leq 135°$ were measured followed by a measurement of the hkl and $hk\bar{l}$ reflections within these limits, giving up to three measurements of an individual reflection. Averaging of equivalent reflections[7] led to 833 reflections that were considered to be observed and used in the analysis.

The structure was solved by locating the V–V vectors in the Patterson function and the light atoms in successive Fourier syntheses. The structure was refined by least-squares methods using isotropic and then anisotropic thermal parameters for all atoms. The final R index was 0.067 for only the observed reflections.

The crystal consists of VO(salpn) molecules packed so that the vanadyl oxygen atom of one molecule occupies the sixth position about the V atom in a neighboring molecule. The result is an infinite chain of molecules about a twofold screw axis linked by $\cdots$V–O–V$\cdots$ bonds. The geometry and atomic numbering are shown in Figure 1. The V–O3′ (and V′–O3 in Figure 1) bond of 2.213 (9) Å which links the molecules is only slightly shorter than the V–O (water molecule *trans* to the vanadyl oxygen) distance of 2.235 (5) Å found in $[OV(H_2O)_4SO_4]H_2O$[8] or slightly longer than the V–N distance of 2.184 (12) Å found for a pyridine

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[1] P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thieleit, *J. Prakt. Chem.*, **149**, 217 (1937).

[2] D. Bruins and D. L. Weaver, *Inorg. Chem.*, **9**, 139 (1970), and references therein.

[3] B. H. Bersted, R. L. Belford, and I. C. Paul, *ibid.*, **7**, 1557 (1968), and references therein.

[4] R. C. Petterson, *Acta Crystallogr., Sect. B*, **25**, 2527 (1969).

[5] N. D. Chasteen, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **8**, 408 (1969).

[6] The small amount of long, thin needles available made the measured density less accurate.

[7] The averaging of the equivalent reflections hkl and $hk\bar{l}$ might introduce a small error in some reflections because of the anomalous scattering of vanadium. However, since the average consists of two values of hkl and one of $hk\bar{l}$, the effect is minimized. An evaluation of the effect of anomalous scattering will be carried out shortly.

[8] C. J. Ballhausen, B. F. Djurinskij, and K. J. Watson, *J. Amer. Chem. Soc.*, **90**, 3878 (1968).

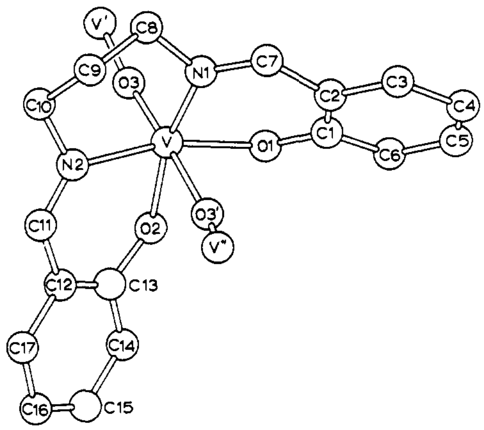

Figure 1. A view of the VO(salpn) molecule illustrating the atomic numbering. The atoms V′, O3′, and V″ are from neighboring molecules and show the polymeric nature of the compound. The pertinent angles are O3-V-O1, 104.0; O3-V-O2, 103.3; O3-V-N1, 94.0; O3-V-N2, 94.5; O3-V-O3′, 168.8; O1-V-O2, 86.3; 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 ν(V=O) appears at 854 cm^{-1} as a very intense absorption. Since the ν(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 ν(V=O) frequency reported to date. Ginsberg[11] has tentatively suggested that low ν(V=O) frequencies may be due to bridging vanadyl groups, although no structural data are available. We are currently investigating VO(2,2′-bipyridine)Cl_2 and VO(1,10-phenanthroline)Cl_2, which also have low ν(V=O) frequencies.[12] Since the low ν(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

$$n\mathrm{CsNiCl_3(s)} = \mathrm{(NiCl_3)_n^{n-}(soln)} + n\mathrm{Cs^+(soln)} \quad (1)$$

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

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

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