CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY AND MATERIALS RESEARCH LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Electron Magnetic Resonance of Oriented Vanadyl Ions in Single Crystals of Palladium *trans*-Bis(benzoylacetonate) and Zinc *cis*-Bis(benzoylacetonate) Ethanolate[1]

BY MICHAEL A. HITCHMAN AND R. LINN BELFORD

Received August 27, 1968

Successful preparation and electron paramagnetic resonance of vanadyl ions (VO^{2+}) substituted in unique orientations into single crystals of palladium *trans*-bis(benzoylacetonate) and zinc *cis*-bis(benzoylacetonate) ethanolate are described. There is circumstantial evidence that the species studied are the *cis* and *trans* forms of vanadyl bis(benzoylacetonate), of which only the *cis* isomer was previously known. The orientations of the principal axes of the **g** tensors suggest that each vanadyl complex is tilted relative to the corresponding host molecule; in the palladium lattice this rotation is such as to move the vanadyl oxygen atom directly away from a neighboring methyl group. The bonding parameters estimated from these data indicate that the π-type orbitals $d_{x^2-y^2}$, d_{xz}, and d_{yz} are fairly ionic and that the σ-type orbital, d_{xy}, is significantly more covalent. The electronic spectrum of the vanadyl ion could not be measured in the Pd lattice, but in the Zn lattice band maxima occurred at 12,700, 16,300, and 20,800 cm^{-1}. If the band at 12,700 cm^{-1} is derived from the transitions $d_{x^2-y^2} \rightarrow d_{xz}$, d_{yz} and that at 16,300 cm^{-1} is from $d_{x^2-y^2} \rightarrow d_{xy}$, the epr measurements are most easily interpreted. The g values of the vanadyl complex in the palladium lattice suggest a similar ordering of the excited states. The in-plane g and hyperfine anisotropy observed for each complex can be explained adequately by a slight admixture of $d_{3z^2-r^2}$ into the ground state, and the sign of the mixing coefficient suggests that the presence of the chelate rings perturbs the ground-state orbital of the metal ion in the same sense as would negative charges on the internal bisector of the chelate rings.

Introduction

Epr spectroscopy can provide much useful information on the bonding in paramagnetic complexes and a number of vanadyl compounds have been studied by previous workers using this technique.[2] Owing largely to a lack of suitable host lattices, however, most of these investigations have been carried out in liquid or frozen solution. Consequently, it has seldom been possible to resolve small anisotropies in the **g** and hyperfine tensors and it is often the small in-plane **g** and hyperfine anisotropies which give the most information on the effective ligand field symmetry in a complex. Moreover, solution measurements yield no information on the orientations of the **g** and **A** tensors in a molecule.

We report here the results of our studies on the epr spectra of vanadyl ion introduced as a slight impurity into the crystal lattices of *trans*-Pd(benzac)$_2$ and *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$ (benzac ≡ the benzoylacetonate anion $CH_3COCHCOC_6H_5^-$; C_2H_5OH ≡ coordinated ethanol; *cis* and *trans* refer to the relative positions of the benzene rings in the complexes). A discussion of the probable orientations and structures of the paramagnetic molecules in the host lattices will be followed by an interpretation of the epr parameters in terms of the energy levels, bonding parameters, and ligand field symmetries of the vanadyl complexes.

Experimental Section

Preparation of Complexes.—*cis*-VO(benzac)$_2$ and large golden needles of *trans*-Pd(benzac)$_2$ were prepared as prescribed by Hon, *et al.*[3] The mixed palladium–vanadyl crystals were obtained as long needles by allowing an oxygen-free chloroform solution of a 3:1 mixture by weight of *trans*-Pd(benzac)$_2$ and *cis*-VO(benzac)$_2$ to diffuse slowly into ethanol. Small diamond-shaped crystals were also obtained, but the vanadyl concentration in these was insufficient for the accurate measurement of their epr spectra. The epr line width suggests that the V:Pd ratio was less than ~0.02.

Zinc acetate (5.4 g) was dissolved in the minimum of water and added to a saturated aqueous solution of sodium hydroxide (2 g). The resulting precipitate of zinc hydroxide was filtered, washed, and suspended in 20 ml of a 1:1 mixture of water and ethanol. Benzoylacetone (8 g) was added to this suspension and the mixture was boiled gently for 10 min. The resulting thick white precipitate was recrystallized from the minimum of hot ethanol to yield large colorless needles. These lost ethanol on exposure to the atmosphere for several days and were, therefore, stored in a bottle containing a piece of filter paper soaked in ethanol.

Large pale green crystals of the mixed complex were obtained by dissolving *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$ (3 g) and *cis*-VO(benzac)$_2$ (1 g) in a slight excess of oxygen-free ethanol and allowing the solution to concentrate slowly in a desiccator containing calcium chloride. From the optical density of the electronic spectrum due to the vanadyl species we estimated the ratio V: Zn in the crystals as ~0.01.

Measurement of Spectra.—The spectra were measured at room temperature with a Varian 4502-12 spectrometer operating at 35 GHz (Q band). The magnetic field was read from a Varian Fieldial accessory; a speck of powdered DPPH was used as a reference in the determination of g values, the isotropic g value of the free radical being taken as 2.0036. The crystals were oriented by placing them upon well-developed faces on a quartz rod and screwing it into the cavity. The direction of the field was varied by rotating the magnet.

trans-Pd(benzac)$_2$ belongs to the space group $P2_1/c$ and crystallizes with the [101] direction as the needle axis and the (111) faces well developed.[3] When the epr spectrum was measured with the magnetic field rotating in the (101) plane,

---

[1] Supported by Advanced Research Projects Agency Contract SD-131 through the Materials Research Laboratory at the University of Illinois, the University of Illinois Graduate Research Board, and the National Science Foundation.

[2] See the review by B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).

[3] P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965), and P. K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, **6**, 730 (1967).

two sets of eight lines each were observed, owing to the interaction of the unpaired electron with the vanadium nuclear spin of $I = {}^7/_2$ for each of the two inequivalent positions in the unit cell. These coalesced into a single set of lines when the magnetic field was along [010] (*b*) or the [101] direction, as required in the space group $P2_1/c$, in which the two molecules of the unit cell have identical projections on the (010) face. Measurements were taken also with the magnetic field rotating in the $(11\bar{1})$ plane.

cis-Zn(benzac)$_2\cdot C_2H_5OH$ also belongs to the space group $P2_1/c$ and crystallizes with *b* [010] as the needle axis and (100) and (001) as the well-developed faces. Epr spectra were measured with the magnetic field vector rotating in the (100), (010), and (001) crystallographic planes. In general, the spectra of VO^{2+} in the Zn lattice appeared quite similar to those in the Pd lattice.

Analysis of Data. A. Definition of Axes.—In order to relate the **g** and A tensors to the molecules we must in each case define a molecular coordinate system.[4] Our choices, illustrated in Figure 1, are as follows.

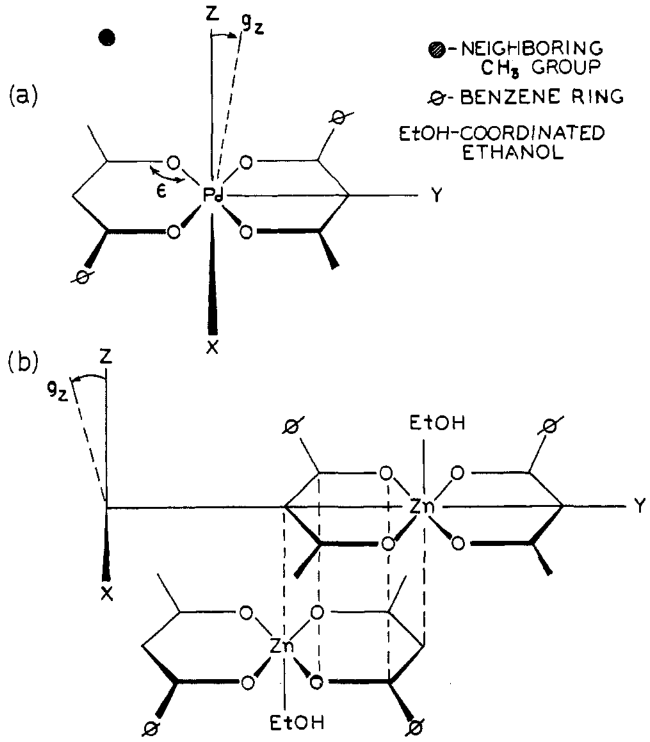

Figure 1.—A diagrammatic representation of the molecular structure of (a) Pd(benzac)$_2$ and (b) Zn(benzac)$_2\cdot C_2H_5OH$, with the axes used to define the **g** and A tensors. The nearest neighbor contacts and the directions found for g_z are also shown.

For *trans*-Pd(benzac)$_2$ the *y* axis is defined from the metal atom to the midpoint of the two oxygen atoms of one chelate ring, the *x* axis being at right angles to this and in the plane of these three atoms. Both *cis*-Zn(benzac)$_2\cdot C_2H_5OH$[5] and *cis*-VO(benzac)$_2$[2] have structures which are close to square pyramidal. For these (and for *trans*-VO(benzac)$_2$, which probably has a similar structure) the *y* axis is defined from the midpoint of the two oxygen atoms of one chelate ring to the midpoint of the other two chelate oxygen atoms, with the *x* axis at right angles to this and in the plane of the four chelate oxygen atoms and the *z* axis orthogonal to *x* and *y* and essentially along the fifth metal–oxygen bond.

The *x*, *y*, *z* coordinates in the two molecules of the unit cell are related to the crystal coordinates as follows, where *X*, *Y*, and *Z* are coordinates in the orthonormal crystal axis system based on *a*, *b*, and *c**

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0.9996 & 0.0133 & -0.0249 \\ -0.0173 & 0.9855 & -0.1687 \\ 0.0223 & 0.1691 & 0.9853 \end{bmatrix} \begin{bmatrix} X \\ \pm Y \\ Z \end{bmatrix}$$

for the Pd lattice, and

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0.9023 & 0.1653 & 0.3982 \\ -0.4311 & 0.3604 & 0.8272 \\ 0.0067 & 0.9181 & -0.3964 \end{bmatrix} \begin{bmatrix} X \\ \pm Y \\ Z \end{bmatrix}$$

for the Zn lattice.

B. Calculation of *g* and *A* Values.—The epr data were analyzed by a method which has been described in detail elsewhere,[4] using a specially written computer program. In essence, measured values of g^2 and g^2K^2 (where *K* is the hyperfine splitting in cm^{-1}) for rotations of the magnetic field vector in different crystallographic planes were fitted to the usual equations by a least-squares technique, and these were solved to give the tensors $\mathbf{g}^2$ and $\mathbf{g}^2\mathbf{K}^2$ expressed in the coordinate systems of the host molecules. These tensors were then diagonalized by unitary transformations to give the principal *g* and *A* values and the Euler angles relating these to the axes of the host molecules.

At least three independent sets of experimental results are required to calculate the *g* and *A* values and, in general, two sets are obtained from each rotation in a crystal plane for the space group $P2_1/c$. However, these two sets are not independent for rotations in planes containing the *b* axis or, of course, for the *ac* plane. The data obtained from the rotations in the (101) and $(11\bar{1})$ planes of *trans*-Pd(benzac)$_2$ were, therefore, sufficient to define the *g* and *A* values, while rotations in (100), (010), and (001) were required for *cis*-Zn(benzac)$_2\cdot C_2H_5OH$. Two or three independent rotations were made in each plane to minimize the errors involved in the mounting of the crystals.

C. Errors.—Errors in the Euler angles were estimated by calculating *g* and *A* from different independent sets of data and comparing the resulting Euler angles. We found that the large difference (~10:1) between the maximum and minimum values of g^2K^2 resulted in rather large uncertainties (5–10%) in the in-plane hyperfine constants calculated by diagonalizing the tensor $\mathbf{g}^2\mathbf{K}^2$. Fortunately, for both complexes it was possible to measure experimentally the hyperfine constants approximately along the directions found for g_x and g_y. For *trans*-Pd(benzac)$_2$, in which the experimentally measured values of A_x and A_y were almost identical, diagonalizing $\mathbf{g}^2\mathbf{K}^2$ gave principal in-plane *A* directions rotated considerably from the *g* directions and with an appreciable anisotropy (~5 G) between A_x and A_y. However, the rms errors in *A* were much larger than in the Zn lattice and could completely absorb the calculated anisotropy. For *cis*-Zn(benzac)$_2\cdot C_2H_5OH$, in which these values were significantly different, the directions and magnitudes of A_x and A_y calculated by diagonalizing $\mathbf{g}^2\mathbf{K}^2$ agreed reasonably well with the experimentally measured values. Study of the errors in each measurement suggests that when the tensor $\mathbf{g}^2\mathbf{A}^2$ is nearly axially symmetric, with a very large axial:equatorial ratio, calculation of A_x and A_y by diagonalizing $\mathbf{g}^2\mathbf{K}^2$ tends to introduce a false anisotropy into the principal in-plane *A* values. For both complexes, therefore, we give those values of A_x and A_y which we measured experimentally along the directions found for g_x and g_y. This means that the in-plane *A* anisotropy might be slightly larger than that reported here, if the principal *A* directions do not, in fact, coincide with the principal *g* directions.

---

(4) M. A. Hitchman and R. L. Belford, paper presented at the Symposium on ESR of Metal Chelates, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 3, 1968; published in "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, Chapter 7.

(5) R. L. Belford, N. D. Chasteen, M. A. Hitchman, P. K. Hon, C. E. Pfluger, and I. C. Paul, *Inorg. Chem.*, in press.

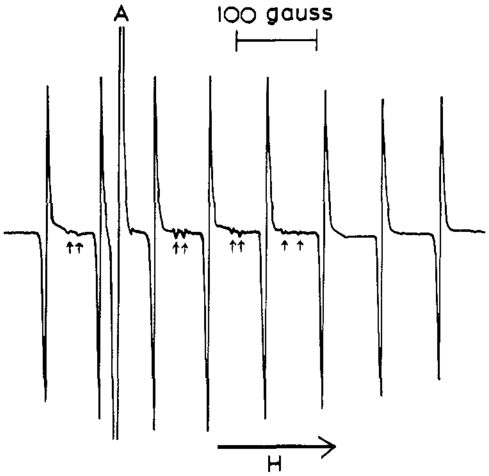

Figure 2.—The epr spectrum of vanadyl-substituted *trans*-Pd(benzac)$_2$ with the magnetic field along the *b* axis. The peak A is due to DPPH. The small arrows point to forbidden hyperfine lines.

Results

Spectrum.—A typical spectrum, for VO^{2+} in the Pd lattice with the magnetic field along the *b* axis, is shown in Figure 2. Line widths in both lattices were about 3 G.

Twinning.—When the magnetic field was rotated in the $(11\bar{1})$ plane of the Pd lattice, four sets of eight lines appeared, with one pair of sets being considerably more intense than the other pair. These lines coalesced into a single set when the field was in the [101] direction and two sets of equal intensity when the field was rotated 90° from this direction. This behavior is identical with that described in detail elsewhere for Cu^{2+} diluted into the needle crystals of *trans*-Pd(benzac)$_2$[4] and is consistent with the needle crystals' of the palladium complex being twinned about a $(10\bar{1})$ face, this face being $(10\bar{1})$ for one twin and $(\bar{1}01)$ for the other. No twinning was evidenced in the Zn lattice.

"Forbidden" Lines.—When the magnetic field vector was close to the molecular *xy* plane (see following section for a precise definition of the *x* and *y* axes) several very weak lines appeared in pairs between adjacent "allowed" lines and were apparently most intense near the center of the spectrum (see Figure 1; when the magnetic field lies along the *b* axis, it is at an angle of $\sim 7°$ to the direction found experimentally for g_y). They belong to the set of 14 possible transitions in which $|\Delta M_S| = |\Delta M_I| = 1$ and which owe their intensity to a combination of the nuclear quadrupole and nuclear Zeeman effects. We have observed these effects in a number of VO^{2+} and Cu^{2+} chelates; at a later date we (H.-S. So and R. L. Belford) will report their detailed behavior and the information, notably electric field gradients, that can be obtained from them.

A and g Tensors.—The principal *g* and *A* values and the Euler angles are listed in Table I.

Discussion of Spectra

Orientations of Guest Molecules.—As the Euler angles only relate the principal *g* directions to the *host* molecules, we must consider both the probable position of the *g* axes in each vanadyl molecule and the orientation of this molecule in the host lattice.

It is fairly certain that in each case, g_z lies along the vanadium–oxygen bond of the vanadyl group. The directions of the in-plane *g* values in each vanadyl complex will depend on the detailed ligand field symmetry. However, as we have shown elsewhere,[6] there are good theoretical reasons for believing that the directions of g_x and g_y should lie fairly close to (within $\sim 15°$ of) the *x* and *y* axes defined for each vanadyl complex; this will be discussed in more detail in a later section.

The Euler angles (Figure 2) show that the in-plane *g* directions lie quite close to the axes defined for the host molecules and this is certainly consistent with the vanadyl substitution's in each case occurring with little reorientation in the *xy* plane and with the g_x and g_y directions' also lying near the *x* and *y* axes of each vanadyl complex.

Configuration of the Paramagnetic Molecules in the Host Lattices. A. Structure.—As the rings are *cis* both in solid VO(benzac)$_2$ and in Zn(benzac)$_2 \cdot C_2H_5OH$, it seems safe to suppose that the vanadyl complex substituted into the zinc lattice is the *cis* isomer. We must, however, consider whether the vanadyl complex substituted into Pd(benzac)$_2$ is *trans*, as in the molecules of the host lattice, or *cis* as in the pure parent vanadyl compound.

There seems to be no good reason why *trans*-VO(benzac)$_2$ should be inherently unstable. Available evidence suggests that the phenyl groups do not produce any great difference between the coordinating ability of the two oxygen atoms of the benzac ligand,[4] so that the ligand field stabilization energies of the *cis* and *trans* isomers should be comparable. The existence of only the *cis* form of VO(benzac)$_2$ in the solid state is probably a crystal-packing effect. It is noteworthy that the vanadyl and zinc benzac complexes, which are five-coordinate, are packed in a rather similar manner[3,5] and are both *cis* while the four-coordinate benzac complexes of Cu and Pd have quite different packing properties and are both *trans*. The methyl groups in *trans*-Pd(benzac)$_2$ are fairly close (3.1, 3.65, 2.75, and 3.9 Å) to atoms of neighboring molecules. It is therefore unlikely that a methyl group could be replaced by a benzene ring (as, in principle, it would have to be if a molecule of *cis*-VO(benzac)$_2$ were to replace one of *trans*-Pd(benzac)$_2$) without a considerable reorientation of the vanadyl molecule relative to the surrounding lattice. Possibly, a rotation of the vanadyl complex in the *xy* plane could occur. The Euler angles, however, suggest that the vanadyl complex is oriented in a

---

(6) M. A. Hitchman, C. D. Olson, and R. L. Belford, *J. Chem. Phys.*, **50**, 1195 (1969).

TABLE I

Host lattice	A_x[a]	A_y	A_z	Angle between A_z and z axis, deg		
trans-Pd(benzac)$_2$	−61.4	−62.1	−164.3	−8.5 ± 0.2		
cis-Zn(benzac)$_2 \cdot C_2H_5OH$	−55.3	−60.5	−164.8	13.4 ± 0.2		
	g_x[b]	g_y	g_z	Ω_1,[c] deg	Ω_2, deg	Ω_3, deg
trans-Pd(benzac)$_2$[d]	1.9829	1.9807	1.9432	−8.4 ± 3.0	−9.8 ± 0.2	7.5 ± 3.0
cis-Zn(benzac)$_2 \cdot C_2H_5OH$[e]	1.9805	1.9758	1.9408	7.9 ± 0.5	14.9 ± 0.2	3.7 ± 1.5

[a] The subscripts x, y, and z refer to the molecular axis closest to the principal g or A value; A_x and A_y are the hyperfine parameters measured along the direction of g_x and g_y. The A values are given in units of 10^{-4} cm^{-1}, with an estimated error in each of $\pm 10^{-4}$ cm^{-1}. [b] The rms error in each g value is ±0.0009 for the Pd lattice and ±0.0007 for the Zn lattice. [c] The Euler angles are defined as follows: to convert the molecular axes into the principal g axes rotate about z by Ω_1 to give $x'y'z$, then by Ω_2 about x' to give $x'y''z'$, and then by Ω_3 about z' to give $x''y'''z'$, each rotation being counterclockwise as viewed from the positive octant. [d] A total of 49 independent measurements were used, 22 of them from rotations in the (101) plane and 27 from rotations in (111). [e] A total of 59 measurements were used, 18 from the (010) plane, 17 from (001), and 24 from (100).

rather similar manner to the palladium complex, the only significant difference being that the z axis of the former compound is rotated through ~10° in the zy plane relative to that of the palladium compound; virtually no rotation seems to occur in the xy plane. It therefore seems probable but not proven that the vanadyl complex studied in the palladium lattice is indeed *trans*-VO(benzac)$_2$.

B. Packing of Guests with Hosts.—The closest intermolecular contact of the palladium atom (which lies on an inversion center) in *trans*-Pd(benzac)$_2$ involves two methyl groups at a distance of 3.75 Å. These are on a line which is approximately in the (101) crystallographic plane and makes an angle of 38.5° with the [10$\bar{1}$] direction.[3] The z axes of the palladium and substituted vanadyl molecules both also lie essentially in the (101) plane and make angles of 17.5 and ~7.5°, respectively, with the [10$\bar{1}$] direction. These facts suggest that the vanadyl molecule is tilted to move the oxygen atom of the VO^{2+} entity directly away from its nearest-neighbor methyl group. The position of the methyl group and observed rotation of g_z are illustrated in Figure 1a. Indeed, if the palladium atom were directly replaced by the vanadium atom, with the vanadyl oxygen bond along the z axis defined for the palladium complex, the carbon–vanadyl oxygen distance would be 2.35 Å, which is much less than the sum of their van der Waals radii (~3.4 Å). The observed rotation *alone* would only increase the oxygen–carbon distance to ~2.6 Å, so that there is probably an accompanying translational displacement and possibly also some reorientation of the neighboring palladium molecules. It is quite surprising that a square-planar complex can be replaced by one having a square-pyramidal structure. Since the metal atom in *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$ is five-coordinate, one might expect that on substitution the vanadyl complex would experience little steric interference from the surrounding lattice. The Euler angles, however, suggest that the z axis of each vanadyl molecule is rotated through ~14° in the zy plane from the z axis of the corresponding zinc molecule, while a rotation of ~11° in the xy plane is also indicated (though this is much less accurately defined). The molecules of *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$ occur in loosely bound pairs, with the molecules in each pair related by an inversion center.[5] Figure 1b gives a diagram of the pairing, together with the rotation observed for g_z. One chelate ring in each molecule experiences rather close intermolecular contacts (3.24–3.34 Å) as indicated by dotted lines in the figure. Each zinc atom appears to be weakly coordinated (3.34 Å) to a carbon atom of the aromatic chelate ring system of its neighbor. It is possible that the vanadyl molecules are oriented in the zinc lattice so as to lessen this interaction somewhat. It may be noted that in solid *cis*-VO(benzac)$_2$ the molecules also occur in similar loose pairs but with a larger distance (3.85 Å) from the vanadium atom to the carbon atom in the neighboring chelate ring.[3,5] Moreover, substitution of VO for Zn·C_2H_5OH eliminates a hydrogen bond[5] and so alters the local packing.

Interpretation of the g and A Values

The shift in the g values of metal complexes from that of the free electron is caused by the mixing of excited electronic states into the ground state by spin–orbit coupling and, in certain point groups, by low-symmetry components of the ligand field.

In the vanadyl complexes studied here the ligand field has a dominant C_{4v} part, with a chelate-ring perturbation which reduces the symmetry to C_{2v} and with the intrinsic asymmetry of the bidentate ligand, *i.e.*, the nonequivalence of methyl and phenyl groups, in each case lowering the symmetry even further. In *trans*-VO(benzac)$_2$ the effect of ligand asymmetry is to produce an along-the-bonds perturbation which will cause the principal in-plane g directions to be rotated away from the x and y axes. As has already been mentioned, the Eulerean angles suggest any such rotation to be very small. Moreover, in *trans*-Cu(benzac)$_2$ no such rotation was observed[4] although it has been shown theoretically that this effect is expected to be much more pronounced for the copper complex than for the vanadyl compound.[6] It therefore seems likely that for the purposes of this discussion the phenyl group in the benzac ligand produces no discernible difference between the coordinating abilities of the two oxygen atoms of the chelate ring and that the *effective* point group of both *cis*- and *trans*-VO(benzac)$_2$ is thus C_{2v}. The validity of this approximation gains support from the fact that the values of $g_x = 1.985$, $g_y = 1.979$, and $g_z = 1.943$ measured for VO(acac)$_2$ (acac is the acetylacetonate anion, $CH_3COCHCOCH_3^-$) in frozen toluene are very similar to those found for the vanadyl benzac complexes[7] (the principal g directions could not be obtained from the frozen solution measurements; the assignments given for VO(acac)$_2$ are those assumed by analogy with the benzac complexes).

The methods by which the g values are related to the covalency and excited electronic states in metal complexes are well established[1] and we have given elsewhere[6] a general calculation of the expression for the in-plane g values of vanadyl complexes of C_{2v} or C_2 symmetry.

Since $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ belong to the same representation of C_{2v}, the ground state of the vanadium ion is given by

$$\psi = a|x^2 - y^2\rangle + b|3z^2 - r^2\rangle$$

in the crystal field approximation. Here the coefficient b is small, as $|3z^2 - r^2\rangle$ is mixed into the ground state by the C_{2v} perturbation upon the strong C_{4v} field. Covalency can be allowed for by forming simple molecular orbitals (MO's), giving a ground state

$$\psi_1 = \alpha(a|x^2 - y^2\rangle + b|3z^2 - r^2\rangle) - \alpha'|L_1\rangle$$

and excited states

$$\begin{aligned}\psi_2 &= \beta|xy\rangle - \beta'|L_2\rangle\\ \psi_3 &= \gamma|xz\rangle - \gamma'|L_3\rangle\\ \psi_4 &= \delta|yz\rangle - \delta'|L_4\rangle\\ \psi_5 &= \eta(-b|x^2 - y^2\rangle + a|3z^2 - r^2\rangle) - \eta'|L_5\rangle\end{aligned}$$

where $|L_1\rangle$, $|L_2\rangle$, etc., represent the appropriate combinations of ligand symmetry orbitals and α, α', etc., are the normalized MO coefficients. Spin-orbit coupling is applied to first order, mixing the excited states ψ_2, ψ_3, and ψ_4 into the ground state ψ_1. Finally, the operator $\beta_e \mathbf{H} \cdot (\mathbf{L} + 2.0023\mathbf{S})$ is applied, where $\mathbf{H}$ is the applied field, and the resulting determinantal equation is solved to obtain the g values. The expressions for the g and A values are given in eq 1a–1f below and are essentially those quoted by McGarvey in his eq 156[2] except that covalency is here taken into account and the terms in b^2 are ignored

$$\Delta g_z = 8a^2\Delta_{xy} \tag{1a}$$

$$\Delta g_x = 2a(a + 2\sqrt{3}b)\Delta_{xz} \tag{1b}$$

$$\Delta g_y = 2a(a - 2\sqrt{3}b)\Delta_{yz} \tag{1c}$$

$$A_z = P\left\{-K - \frac{4}{7}a^2\alpha^2 - \frac{1}{14}\,\frac{3a + \sqrt{3}b}{a - \sqrt{3}b}\Delta g_y - \frac{1}{14}\,\frac{(3a - \sqrt{3}b)\Delta g_x}{a + \sqrt{3}b} - \Delta g_z\right\} \tag{1d}$$

$$A_x = P\left\{-K + \frac{2}{7}a^2\alpha^2 - \frac{4\sqrt{3}}{7}ab - \Delta g_x + \frac{1}{14}\,\frac{(3a + \sqrt{3}b)\Delta g_y}{a - \sqrt{3}b} - \frac{1}{7}\,\frac{b}{a}\Delta g_z\right\} \tag{1e}$$

$$A_y = P\left\{-K + \frac{2}{7}a^2\alpha^2 + \frac{4\sqrt{3}}{7}ab - \Delta g_y + \frac{1}{14}\,\frac{(3a - \sqrt{3}b)\Delta g_x}{a + \sqrt{3}b} + \frac{1}{7}\,\frac{b}{a}\Delta g_z\right\} \tag{1f}$$

where $\Delta g_q = 2.0023 - g_q$, $\Delta_{xy} = \alpha^2\beta^2\xi/E_{xy}$, $\Delta_{xz} = \alpha^2\gamma^2\xi/E_{xz}$, and $\Delta_{yz} = \alpha^2\delta^2\xi/E_{yz}$. ξ is the spin–orbit coupling constant of the vanadium ion *in the complex*, K is the isotropic hyperfine constant in the complex, and P is given by the expression $P = 2.0023g_N\beta_e\beta_N \cdot \langle r^{-3}\rangle$. The terms E_{xy}, E_{xz}, and E_{yz} are the energies (relative to the ground state) of the excited states in which the unpaired electron is principally in the d orbital denoted by the subscript.

In the derivation of the above equations it should be realized that no explicit account has been taken of the unpaired electron density on the ligands and that the overlap between the ligand and metal orbitals has been set to zero.[8] For copper complexes, expressions are often used in which these ligand terms have been included;[2,9] for *trans*-Cu(benzac)$_2$ ~6% of the g shift is, in fact, due to the ligand unpaired electron density.[4] However, for vanadyl complexes, the uncertainty in the knowledge of ξ, P, and the appropriate overlap integrals means that the inclusion of these ligand terms is probably not justified, provided that α^2, β^2, γ^2, and δ^2 are interpreted as net metal orbital populations.

It can be seen that the g and A values depend essentially on three things: (1) the sizes of ξ and P, (2) the covalency parameters α, β, γ, and δ and the mixing coefficient b, and (3) the energies of the excited states. The coefficient b is very small and it contributes significantly only to the *anisotropy* of the in-plane g and hyperfine values (*i.e.*, when it adds to g_x, it subtracts equally from g_y, providing $\Delta_{xz} \approx \Delta_{yz}$). We can therefore use average values of the in-plane g and hyperfine parameters and neglect the $d_{3z^2-r^2}$ mixing, to calculate approximate MO coefficients and excited-state energies of the complexes and then use these in the full expressions including b to interpret the completely anisotropic g and A values. It is, however, first necessary to choose the constants ξ and P; many attempts have been made to estimate these. The spin–orbit coupling parameter probably is not very far from the value $\xi = 170$ cm^{-1} (the value for V^{2+}, 3d^3) used by Kivelson and Lee.[10] In the absence of other information, we will use a fixed relationship between ξ and P

---

[7] R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).

[8] K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965), as well as ref 2, eq 140, give the complete expressions for $g_\perp$, $g_\parallel$, $A_\perp$, and $A_\parallel$ of vanadyl systems for the cases where the **g** and **A** tensors have coincident axial symmetry (requiring $a = 1$, $b = 0$) and the ligand and overlap terms are explicitly included.

[9] B. W. Moores and R. L. Belford, Abstracts, 155 National Meeting of the American Chemical Society, San Francisco, Calif., April 2, 1968 No. S106; also, B. W. Moores, Ph.D. Thesis, University of Illinois, 1968.

[10] D. Kivelson and S.-K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964); see T. M. Dunn, *Trans. Faraday Soc.*, **157**, 1441 (1961), for a tabulation of spin–orbit coupling parameters, and A. J. Freeman and R. E. Watson in "Magnetism" Vol. IIA, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1965, pp 167–305, for a tabulation of $\langle r^{-3}\rangle$ values from which P can be obtained for various states of ionization.

$$\xi \approx 18{,}200P - 56\ \text{cm}^{-1} \qquad (2)$$

obtained by fitting the ξ and P values[10] for the configurations d^{5-n} of V^{n+} and adding 8 cm^{-1} to ξ to take account of some increase of effective vanadium atom charge in the excited states. (Strictly, the parameter α^2 appearing in the hyperfine expressions should be interpreted as the square of an MO coefficient, while the α^2 appearing in the g expressions should be interpreted as a metal orbital population. The use of a slightly different effective P would adjust for this discrepancy, but the probable discrepancy is sufficiently small and the other uncertainties are sufficiently large that we doubt that such an adjustment would be warranted.)

If the excited-state energies are known, it is now possible to use eq 1a–1f with eq 2 to calculate approximate MO coefficients for the complexes. As there is still considerable controversy over the ordering of the excited states in vanadyl ketoenolato complexes, it is interesting to compare the coefficients obtained by using the various energy level schemes which have been proposed to interpret the electronic spectra of these compounds.

Ordering of the Excited States. A. Alternatives.—Basically, three energy level schemes, which we shall label I, II, and III, have been proposed for vanadyl complexes. The schemes will be considered only in relation to the epr results; other arguments for and against each scheme are discussed in Selbin's review article[11] and the recent paper by Ballhausen, Djurinskiy, and Watson[12] and the references therein. (I) Bands at $\sim$23,000 cm^{-1} are due to $d_{x^2-y^2} \rightarrow d_{z^2}$, those at $\sim$16,500 cm^{-1} to $d_{x^2-y^2} \rightarrow d_{xy}$, and those at $\sim$13,500 cm^{-1} to $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$. (II) Bands at $\sim$23,000 cm^{-1} are charge-transfer or intraligand transitions, those at $\sim$16,500 cm^{-1} are $d_{x^2-y^2} \rightarrow d_{z^2}$, and all three transitions $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$, and d_{xy} occur at $\sim$13,500 cm^{-1}. (III) The bands at $\sim$23,000 and $\sim$16,500 cm^{-1} are assigned as in II, but only $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ are $\sim$13,500 cm^{-1}. The transition $d_{x^2-y^2} \rightarrow d_{xy}$ is assigned to a very weak band which has been reported at $\sim$11,000 cm^{-1} for some vanadyl ketoenolato complexes.

B. Optical Spectra.—We have recorded the electronic spectrum of vanadyl-substituted *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$ as a mull and also in single crystals. The spectrum was weak, but three bands were clearly resolved at 12,700, 16,300, and 20,800 cm^{-1}. The electronic spectrum of the vanadyl ions in *trans*-Pd(benzac)$_2$ could not be obtained because of the absorption due to the palladium ions. Therefore, because of the similarity of the electronic spectra of vanadyl ketoenolato complexes we shall use the band maxima of solid *cis*-VO(benzac)$_2$ at 14,500, 16,700, and 24,400 cm^{-1} [13] to interpret the epr parameters of the species substituted into *trans*-Pd(benzac)$_2$; accordingly, the Pd lattice results are subject to more uncertainty.

C. Derived Bonding Parameters and Implications.—The electronic spectra of the two complexes were assigned according to each of the three schemes and MO coefficients calculated from eq 1a, 1b, 1d, and 1e with the following approximations: $b = 0$, $a = 1$; $\Delta g_x = 2.0023 - 0.5(g_x + g_y)$, $A_x = 0.5(A_x + A_y)$. Thus, γ^2 here represents the MO population of both d_{xz} and d_{yz}. The only MO population altered by changing the electronic spectral assignments is β^2. The calculated coefficients for the two lattices are given in Table II.

While the *absolute* values of the MO coefficients cannot be considered very accurate, largely because of the uncertainty in ξ and P,[14] the *relative* magnitudes are much more meaningful. In particular, as each energy level scheme assigns the transitions $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ to the same spectral region, while altering the assignment of $d_{x^2-y^2} \rightarrow d_{xz}$, the ratio β^2/γ^2 changes drastically from one energy scheme to another. The coefficients of $d_{x^2-y^2}$ and d_{xz}, d_{yz} are in each case close to 1, suggesting nearby ionic character in the bonding involving these orbitals. The coefficient β^2, however, varies from $\sim$0.80 to $\sim$0.52 depending on energy level assignment. Although β^2 might well be somewhat smaller than α^2 and γ^2, as it involves σ rather than π bonding, it should not be very much smaller, and a value of $\beta^2 = 0.75$–0.85 would seem to be reasonable (a value of 0.5 corresponds to a completely covalent bond in the model used here). Typical values found for similar systems are $\alpha^2 = 0.72$–0.95, $\beta^2 = 0.75$–0.84, and $\gamma^2 = 0.92$–~ 1.0 for copper complexes[14,15] and $\alpha^2 = 1.0$ (assumed), $\beta^2 = 0.84$, and $\gamma^2 = 0.90$–0.95 for VO(acac)$_2$.[10] (The coefficients for VO(acac)$_2$ were estimated[10] using formulas including ligand terms; adjustment *via* a Mullikan overlap population analysis yields corrected values $\alpha^2\beta^2 = 0.68$, $\alpha^2\gamma^2 = 0.84$–0.90, and $\beta^2/\gamma^2 = 0.76$–0.81. The full expressions including ligand terms can be reduced to our expressions with only very small corrections providing metal orbital populations, rather than coefficients, are compared.)

Note that if $\alpha^2\xi$ has been estimated incorrectly, its true value is probably larger than that used, or a value of $\gamma^2 > 1$ would be obtained; thus, the calculated values of β^2 are *upper* limits. It therefore seems that the epr data rather strongly support the band assignments of energy level scheme I for the vanadyl benzac complexes, at least as far as the transitions $d_{x^2-y^2} \rightarrow d_{xz}$, d_{yz} and $d_{x^2-y^2} \rightarrow d_{xy}$ are concerned. This conclusion agrees with a recent analysis of the low-temperature polarized crystal spectrum of $VO(H_2O)_5^{2+}$, in which the band at 13,000 cm^{-1} was assigned as $d_{x^2-y^2} \rightarrow d_{xz}$, d_{yz} and that at 16,000 cm^{-1} as $d_{x^2-y^2} \rightarrow d_{xy}$.[12]

---

[11] J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).

[12] C. J. Ballhausen, B. F. Djurinskiy, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 3305 (1968).

[13] M. Valek and R. L. Belford, to be submitted for publication.

[14] The relationship between ξ and P in eq 2 could be altered. For example, using the $\xi = 14{,}500P$, which was employed by G. F. Kokoszka, H. C. Allen, and G. Gordon, *Inorg. Chem.*, **5**, 91 (1966), and which is the same as our eq 2 for $\sim V^{3+}$, d^2, one would obtain smaller values of γ^2 for given values of α^2.

[15] See ref 2, p 148; H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

TABLE II

METAL ORBITAL POPULATIONS AND ISOTROPIC HYPERFINE CONSTANTS

Host lattice	α^2	γ^2 [a]	$\beta^2{}_{\mathrm{I}}/\gamma^2$ [b]	$\beta^2{}_{\mathrm{II}}/\gamma^2$	$\beta^2{}_{\mathrm{III}}/\gamma^2$	b^2	K
trans-Pd(benzac)$_2$	0.92	0.96	0.83	0.72	0.55	0.00024	0.75
cis-Zn(benzac)$_2 \cdot C_2H_5OH$	0.96	0.95	0.82	0.63	0.55	0.00079	0.73

[a] γ here represents the MO coefficient of both d_{xz} and d_{yz}, as average g shifts were used in the calculations; see the text for a definition of the coefficients and the method of calculation. α^2 and γ^2 are determined to within a few per cent; P is arbitrarily set at 0.0123 cm^{-1}, corresponding approximately to $3d^34s^1$ or $3d^{3.3}$ and $\xi = 168$ cm^{-1}. [b] The subscripts represent the energy level scheme used to assign the excited-state energy E_{xy}; see text. The ratio β^2/γ^2 is tabulated because it does not depend on the hyperfine parameters, but only upon $\Delta g_{\parallel}/\Delta g_{\perp}$, $\Delta E_{xz}/\Delta E_{xy}$, and the assumption that one can characterize both transitions involved with a common single value of ξ.

D. Blue-Green Band.—Although the epr data give no direct information on the assignment of the bands at ~23,000 cm^{-1}, the fact that no band in this region was observed for pure *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$ suggests that the peak at 20,800 cm^{-1} in the vanadyl-substituted complex is not due to an intraligand transition. This conclusion is also supported by the fact that peaks corresponding to a progression of ~700 cm^{-1} have been observed[13] on the band at 24,400 cm^{-1} in solid *cis*-VO(benzac)$_2$ at low temperature. Similar progressions have been seen on the lower energy bands in several vanadyl complexes[12,13,16] and are generally believed to be due to the coupling of the electronic transition with the excited-state vanadium–vanadyl oxygen stretch. This leaves the possibilities that the ~23,000-cm^{-1} bands are due to the transition $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$ or that they are charge transfer in origin. Although we are inclined toward the former explanation, no definite choice between the alternatives is yet possible.

The In-Plane Anisotropy. A. g Tensor.—We shall consider first the $g_{\perp}$ anisotropy, as it could be measured considerably more accurately than the small anisotropy in $A_{\perp}$.

Equations 1b and 1c show that two factors contribute to the $g_{\perp}$ anisotropy: (1) the mixing coefficient b of the $d_{3z^2-r^2}$ orbital in the ground state and (2) the difference between the energies and/or MO coefficients of the d_{xz} and d_{yz} orbitals.

It is unlikely that the anisotropy is caused principally by a difference between the d_{xz} and d_{yz} coefficients, as this would cause γ^2 to be appreciably greater than 1. If the anisotropy is caused by an energy separation between d_{xz} and d_{yz}, these levels must be split by ~2000 cm^{-1} and one might expect this to be detected in the electronic spectrum. (For *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$ the predicted energies are $E_{xz} = 11{,}600$ cm^{-1} and $E_{yz} = 14{,}100$ cm^{-1} if $\gamma^2 = \delta^2$ and $\langle 1/E_{xz,\,yz} \rangle = 1/12{,}700$ cm^{-1}.) However, it is possible that one of the transitions is too broad and weak to make it normally visible. As has already been mentioned, a very weak band has sometimes been observed at ~11,000 cm^{-1} in vanadyl ketoenolato complexes, and indeed in the case of VO(acac)$_2$ Yeranos has assigned a very weak band at ~12,000 cm^{-1} to E_{xz}, with E_{yz} being the strong peak at ~14,000 cm^{-1}.[17] Although we admit the possibility that the $d_{x^2-y^2} \rightarrow d_{xz}$ and $d_{x^2-y^2} \rightarrow d_{yz}$ intensities could be very different, we see no clear-cut reason for it.

The most reasonable explanation of the $g_{\perp}$ anisotropy certainly seems to be a slight admixture of $d_{3z^2-r^2}$ into the ground state, particularly as there are good theoretical reasons[6] to believe that when the asymmetric component of the in-plane ligand field lies along the ground-state lobes, as is the case for the perturbation due to the chelate rings in the benzac complexes, the $d_{3z^2-r^2}$ mixing is likely to be the main cause of the $g_{\perp}$ anisotropy. This explanation is also supported by the fact that the anisotropy in similar copper complexes is very much smaller,[4,18,19] and in these the $d_{3z^2-r^2}$ mixing cannot contribute to the $g_{\perp}$ values, as the perturbation from the chelate rings acts along the direction of the ground-state orbital nodes, rather than along the lobes (typical $g_{\perp}$ values for a similar copper complex are those for *trans*-Cu(benzac)$_2$,[4] where $g_x = 2.0489$ and $g_y = 2.0477$).

To estimate the values of b which would give the observed anisotropy, we set $\Delta_{xz} = \Delta_{yz}$ and, as a first approximation, set $a = 1$. Equations 1b and 1c then yield values of $b = -0.0155$ for *trans*-Pd(benzac)$_2$ and $b = -0.0281$ for *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$. The values of b^2 are listed in Table II, and we see that only a very small admixture of $d_{3z^2-r^2}$ into the ground state is required to produce the observed anisotropy. The corrected value of a is given by $a^2 = 1 - b^2$, so that the approximation $a = 1$ is a very good one, and no further correction need be applied to b.

B. Hyperfine Tensor.—We consider next the anisotropy in $A_{\perp}$. If we set $b = 0$, the predicted values of $A_x - A_y$ are 0.33×10^{-4} cm^{-1} for *trans*-Pd(benzac)$_2$ and 0.71×10^{-4} cm^{-1} for *cis*-Zn(benzac)$_2 \cdot C_2H_5OH$; the use of the values of b calculated in the previous section yields $A_x - A_y = 4.2 \times 10^{-4}$ cm^{-1} for the Pd complex and 7.6×10^{-4} cm^{-1} for the Zn one. The observed values are $(0.7 \pm 2) \times 10^{-4}$ and $(5.2 \pm 2) \times 10^{-4}$ cm^{-1}, respectively. The sign and magnitude of the observed anisotropy in the zinc complex are, therefore, in reasonable agreement with the proposed admixture of $d_{3z^2-r^2}$ into the ground state; the result for the Pd lattice is inconclusive.

---

(16) G. Basu, W. Yeranos, and R. L. Belford, *Inorg. Chem.*, **3**, 929 (1964).

(17) W. Yeranos, Ph.D. Thesis, University of Illinois, 1964.

(18) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).

(19) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 915 (1967).

Physically, the $d_{3z^2-r^2}$ mixing has the effect of augmenting the ground-state lobes which are directed along the x axis, while diminishing those along the y axis, or *vice versa*. The negative values of b suggested by the epr data of the vanadyl–benzac complexes means that in these compounds the ground-state lobes along x are augmented, and simple crystal field theory would relate this to a perturbation acting like a negative charge along the y axis. This seems reasonable, as the oxygen hydrid σ orbital which is directed approximately toward the metal atom is probably weighted somewhat more toward the interior than the exterior of the chelate ring. The oxygen orbital involved in the C–O σ bonding is surely directed along the bond, while the one pointing approximately toward the metal ion is probably a hybrid sp^η ($\eta \geq 2$) and so is directed along a line making an angle of 120° or less with the CO bond, whereas the C–O–M angle (ϵ in Figure 1a) is generally ~7° greater than 120° (it is 127.5° in *cis*-VO(benzac)$_2$[3]). Therefore, the ground-state metal orbital lobes along y probably interact more strongly with the occupied ligand σ-bonding orbitals than do those along x.

Acknowledgment.—We wish to thank Dr. Brian Moores for several helpful discussions.

CONTRIBUTION FROM THE CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

The Pentacarbonyls of Ruthenium and Osmium. IV. Synthesis of Alkyl- and Acetylosmium Carbonyls

BY F. L'EPLATTENIER[1]

Received November 4, 1968

The sodium salt Na[OsH(CO)$_4$] has been obtained in high yields by the reduction of OsH$_2$(CO)$_4$ with sodium sand in tetrahydrofuran. The nuclear magnetic resonance and infrared spectra are in agreement with a symmetry C_{3v} and a metal–hydrogen bond. No evidences for the formation of the dianion Os(CO)$_4^{2-}$ were obtained. The monosodium derivative is a strong nucleophilic reagent and reacts with methyl halides to give the new alkyl compounds OsCH$_3$H(CO)$_4$, OsCH$_3$I(CO)$_4$, and Os(CH$_3$)$_2$(CO)$_4$. Nmr and infrared spectra indicate a *cis*-octahedral structure for all three substances. Methylhydridotetracarbonylosmium could not be isolated in a pure state; at room temperature it decomposes very rapidly with evolution of methane. On addition of triphenylphosphine, the decomposition is promoted; Os(CO)$_4$P(C$_6$H$_5$)$_3$ and Os(CO)$_3$(P(C$_6$H$_5$)$_3$)$_2$ are formed, together with some monosubstituted OsCH$_3$H(CO)$_3$P(C$_6$H$_5$)$_3$. The two other alkyl derivatives OsCH$_3$I(CO)$_4$ and Os(CH$_3$)$_2$(CO)$_4$ seem to be thermally very stable. The reaction of OsBr$_2$(CO)$_4$ with methylmagnesium bromide was also investigated. The salt [MgBr]$_2$[Os(COCH$_3$)$_2$Br$_2$(CO)$_2$]·5THF was obtained. Infrared and nmr data suggest an all-*cis* configuration for the anion Os(COCH$_3$)$_2$Br$_2$(CO)$_2^{2-}$.

We have recently reported[2] the synthesis and the identification by nuclear magnetic resonance and infrared spectroscopy of dihydridotetracarbonylosmium, OsH$_2$(CO)$_4$, and some of its substitution products. In the triad Fe, Ru, and Os, very few alkylcarbonyls are known and those of osmium seem to have been completely neglected. This prompted us to carry out the reduction of OsH$_2$(CO)$_4$ with sodium and to investigate the reactivity of the so formed monoanion OsH(CO)$_4^-$ toward methyl bromide and methyl iodide. The following new compounds were identified: methylhydridotetracarbonylosmium, OsCH$_3$H(CO)$_4$, methyliodotetracarbonylosmium, OsCH$_3$I(CO)$_4$, and dimethyltetracarbonylosmium, Os(CH$_3$)$_2$(CO)$_4$.

We also studied the reaction of dibromotetracarbonylosmium, OsBr$_2$(CO)$_4$, with methylmagnesium bromide and isolated the diacetyl anion Os(COCH$_3$)$_2$Br$_2$(CO)$_2^{2-}$. This anionic metal complex is closely related to the anionic alkylmetal carbonyls of the type M(CO)$_5$COR$^-$ (M = Cr, Mo, W) synthesized by Fischer and Maasböl.[3,4]

Experimental Section

All of the preparations described in this paper were carried out under an atmosphere of prepurified nitrogen.

Osmium tetroxide was purchased from Johnson Matthey Chemicals Ltd., London. Hydrogen was analytical grade and carbon monoxide was reagent grade and used without further purification. Tetrahydrofuran was treated with iron(II) sulfate and distilled over sodium and lithium tetrahydridoaluminate. Triphenylphosphine was sublimed before use.

The high-pressure reactions were carried out in a 200-ml stainless steel autoclave, heated in a thermostated oil bath.

The infrared spectra were measured with a Perkin-Elmer instrument, Model 521, equipped with grating. The spectra were recorded on an expanded abscissa scale and calibrated with CO. The limit of accuracy based on instrument specifications and reproducibility of data is believed to be ± 1 cm^{-1}.

---

(1) Department of Chemistry, University of Neuchâtel, 2000 Neuchâtel, Switzerland.

(2) F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).

(3) E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964).

(4) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967).