Electronic spectra for samples in oil mulls consist of three main absorption areas. Assignments are based on an O_h coordination model because of absorption energies,[6] spectral display, and magnetic moments. The split middle band (ν_2) is typical of those dealt with by van Leeuwen.[5] Its calculated[7] energy ($^3A_{2g} \rightarrow {}^3T_{1g}$(F)) was always within the observed range. Based on analytical, magnetic, and spectral evidence, these complexes are pseudo-O_h weak-field cases. Other properties imply they are coordination polymers. Observed and calculated d–d bands, β values, and magnetic moments are listed in Table II.

TABLE II
d–d SPECTRA (kK) AND MAGNETIC MOMENTS FOR SOLID COMPLEXES

Compound	ν_1	ν_2		ν_3	β	Calcd ν_2	μ_{eff}, BM
$Ni(glycol)_2Cl_2$	8.22	12.9	14.2	23.9	0.79	13.6	3.36
$Ni(glycol)_2Br_2$	8.12	12.7	13.8	23.5	0.77	13.4	3.25
$Ni(Me\text{-}gly)_2Cl_2$	7.70	12.7	14.1	23.5	0.82	12.9	3.29
$Ni(Me\text{-}gly)_2Br_2$	7.78	12.5	13.7	23.3	0.80	13.0	3.36
$Ni(Et\text{-}gly)_2Cl_2$	7.65	12.5	14.1	23.4	0.81	12.8	3.35
$Ni(Et\text{-}gly)_2Br_2$	7.47	12.5	13.9	23.0	0.81	12.5	3.32
$Ni(Et\text{-}gly)_2I_2$	7.43	12.1	13.3	...[a]	...	...	3.33
$Ni(glyme)Cl_2$	6.91	11.6	13.2	22.0	0.80	11.6	3.54
$Ni(glyme)Br_2$	6.70	11.1	12.3	21.2	0.76	11.3	3.46
$Ni(glyme)_2I_2$	6.90	11.6		...	...	...	3.27

[a] Unlisted bands are masked by charge-transfer absorptions.

Evidence of extensive band splitting is lacking, indicating a uniform average field. Thus average environment calculations were used to approximate ligand *Dq* values. For bis complexes a NiO_4X_2 format resulted in regular *Dq* decreases with O-alkyl substitution and gave most reasonable magnitudes of *Dq*. Conversely, monoglyme compounds are more agreeable with a NiO_2X_4 coordination type involving bridging halide ions. Both models imply bonding two oxygen atoms per ligand, as in other similar systems.[8–11] A spectrochemical series of glycol (890) > 2-methoxyethanol (860) > 2-ethoxyethanol (810) > glyme (~750) is obtained from average field calculations. We have isolated tris complexes of glycol and 2-methoxyethanol for a companion study and obtain *Dq* values of 887 and 868 cm^{-1} from their mull spectra. These independent results support our calculations well.

Our work substantiates previous measurements from 2-methoxyethanol solutions of nickel bromide[12] and identifies a reported uv–visible spectrum[13] as that of tris(glycol)nickel(II). Pronounced reduction in coordinating ability by O-alkyl substitution is demonstrated by this series. Similar changes for N-alkyl-substituted ethylenediamines[14] are not as extensive in curtailing coordination. Although glycol is slightly better than water as a ligand, remaining members are weaker. This ligand system is comparable to urea, THF, DMSO, substituted and cyclic amides, thiourea, and substituted pyridine N-oxides in terms of donor strengths.

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Correspondence

Bonding by Outer d Orbitals and by Continuum Orbitals in Molecules of Second-Row Atoms

Sir:

Recently Jørgensen[1,2] has made the interesting suggestion that the acceptor properties of the PF_3 group in complexes of transition metals in low oxidation states, for example, $Fe(PF_3)_5$ and $Co(PF_3)_4I$, can be understood in terms of the involvement in bonding of continuum orbitals. Additionally, Jørgensen suggested that the involvement in bonding by 3d orbitals at phosphorus is very small, and *prima facie* this contrasts with the viewpoint that ascribes the acceptor properties of PF_3 in complexes to the availability of the 3d orbitals at phosphorus.[3] The purpose of this letter is to discuss Jørgensen's proposal in relation to the conventional models of bonding based on the overlapping of discrete orbitals of either atomic or molecular character.

In principle, even molecules of phosphorus and sulfur in high coordination states can be accommodated in bonding schemes which neglect 3d orbitals altogether,[4] although recent support for the concept of bonding by 3d orbitals[5] is suggested by the calculations of Boer, Boyd, and Lipscomb[6–8] which use minimum basis sets of

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Slater functions for molecules containing second-row atoms (*e.g.*, H_2S, SiH_4, PH_3, PO, PO_2^-). These calculations show that the introduction of hydrogen-like 3d functions significantly affect the molecular energies and electronic distributions. Moreover, for SO_2 and SO_4^{2-} d-function populations of 1.17 and 2.58, respectively, have been found in calculations with Gaussian basis sets.[9,10] A distinctive feature of these calculations is that attempts were made to find the optimum forms of the 3d orbital functions. It is, however, easy to show that if the 3d functions were not optimized, that is if substantially different basis sets were used for the calculations, then the continuum orbitals (or higher discrete orbitals) could assume an important role.

The continuum orbitals are one-electron wave functions in which the electron is unbound to the positive ion and in which the electronic energy (E) may be any one of a continuously varying set of positive values. In principle, these orbitals extend over all space although, as noted by Jørgensen, they can be combined so that their amplitudes are particularly large in specific regions, such as between two nuclei in a molecule. For a central field potential, the continuum orbitals can be expressed as the product of a radial function $R_{El}(r)$ and the appropriate spherical harmonic $Y_{lm}(\theta,\phi)$.[11] In general, the continuum radial functions R_{El} are needed for expanding an arbitrary radial function, and the general form[12-14] of the expansion is given in eq 1 for the radial function (R_d)

$$R_\mathrm{d} = c_1R_{3\mathrm{d}} + c_2R_{4\mathrm{d}} + c_3R_{5\mathrm{d}} + \ldots + \int_{E=0}^{E=\infty} c_ER_{E2}\,\mathrm{d}E \quad (1)$$

of a d orbital, where the continuum orbitals corresponding to $l = 2$ are appropriate.

A difficulty in making expansions of the type in eq 1 is that usually for many-electron systems the detailed forms of the higher discrete atomic orbitals are not known, although eventually they converge to the hydrogen-like functions. However, for phosphorus in the state of average energy based on the $(3s)^1(3p)^3(3d)^1$ valence configuration, the 3d orbital function[15] has an overlap integral of 0.9818 with the hydrogen atom 3d orbital, and this suggests that the hydrogen atom d orbitals may closely resemble the d functions of phosphorus for the configurations $(3s)^1(3p)^2(n\mathrm{d})^1$. In a representative example, we find when the 3d hydrogen-like function (exponent 1.40) found by Boyd and Lipscomb[6] for PO is expanded in terms of the hydrogen d orbitals according to eq 1, that the discerte hydrogenic d orbitals, and, by implication, the discrete phosphorus d orbitals contribute only slightly; thus $c_1 = 0.189$, $c_2 = 0.134$, and $c_3 = 0.098$, and the main contribution (over 90%) in the expansion comes from the continuum d orbitals. In general, continuum orbitals are forced to contribute strongly in this context when an orbital function is concentrated in different regions of space from all the discrete orbitals in the expansion set.

This example brings out that the extent of involvement by continuum orbitals is intimately related to the particular basis set used for a calculation and that there is an essential equivalence between the model emphasizing continuum atomic orbitals in bonding and the alternative model that allows for atomic orbitals changing in the molecule from their forms in the free atoms. Clearly in no fundamental sense can either of these representations be considered intrinsically better than the other; the choice between them inevitably rests on their relative convenience for making computations and for visualizing the bonding.

For making computations with the model that emphasizes the role of the continuum orbitals, one would have the difficulty of choosing the detailed forms of the one-electron wave functions, and this problem is closely related to that encountered in choosing suitable forms for bound electron wave functions. This is particularly significant for bonding by atomic orbitals which have high energies in the free atoms and which tend to be easily polarized in molecules. Indeed for outer d orbitals it is known that even in atomic configurations the radial functions can be very sensitive to the particular state of the atom,[16,17] and for this reason alone there does seem to be some conceptual advantage in envisaging these orbitals as adopting their optimum forms in molecules.

Some justification for the concept of atomic orbitals in molecules is suggested by noting that, in principle, molecular wave functions converging to the Hartree–Fock limit can be found by minimizing the molecular energy by a complete variation of all radial functions in a basis of atomic orbitals centered on all the atoms in the molecule. This represents a level of refinement which has not yet been reached for calculations on polyatomic molecules containing second-row atoms, and therefore the 3d orbital populations referred to above must be expected to change as the basis sets are extended.[18] In the limit, the relative populations of the 3s, 3p, and 3d orbitals would indicate which of the various approximate bonding schemes[4,5] provides the most helpful description for particular molecules.

The concept of molecular orbitals of a polyatomic fragment within a molecule can be introduced by analogy with that indicated for atomic orbitals in mole-

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cules treated in the one configuration approximation. Likewise continuum orbitals could be invoked in situations where the optimum forms of the molecular orbitals of a molecular fragment change substantially during the process of molecule formation.

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The Crystal Structure of $Yb_{11}Sb_{10}$

Sir:

The compound previously designated as α-Yb_5Sb_4 is the low-temperature form of one of the intermediate phases occurring in the Yb–Sb system investigated by Bodnar and Steinfink.[1] The stoichiometry of the compound had not previously been established with certainty, although a single phase was observed on an X-ray powder diffraction pattern when the elements reacted in a 5:4 ratio. The lattice parameters and space group of this compound indicated that it was isostructural with one of the monogermanide phases reported by Tharp, Smith, and Johnson.[2] A later single-crystal analysis by Smith, Johnson, and Tharp[3] established the structure of this new rare earth germanide phase and showed that the composition corresponded to an 11:10 ratio of the elements.

Procedure.—The preparation of this compound has been described previously.[1] The material is spongy, and single crystals were difficult to find. The single crystal used in this investigation was an irregular fragment with encompassing dimensions of about 0.06 × 0.07 × 0.10 mm^3 and with a shape which could be approximated by six planar faces.

TABLE II
INTERATOMIC DISTANCES IN $Yb_{11}Sb_{10}$[a]

Atom 1	Atom 2	Distance, Å	Esd, Å
Yb(1)	Sb(4)	3.125	0.003
	Sb(2)	3.159	0.006
	Sb(5)	3.413	0.007
	Sb(1)	3.420	0.005
	Sb(5)	3.527	0.007
	Yb(4)	3.701	0.004
	Yb(4)	3.819	0.004
	Yb(3)	3.920	0.005
	Yb(2)	3.910	0.009
	Yb(1)	4.223	0.004
Yb(2)	Sb(1)	2.933	0.010
	Sb(3)	3.464	0.018
	Sb(2)	3.556	0.010
	Sb(5)	3.672	0.011
	Yb(4)	4.319	0.009
	Yb(2)	3.963	0.013
Yb(3)	Sb(3)	3.491	0.016
	Sb(5)	3.465	0.008
	Yb(4)	4.119	0.005
Yb(4)	Sb(5)	3.148	0.007
	Sb(1)	3.165	0.005
	Sb(3)	3.393	0.016
	Sb(4)	3.176	0.003
	Yb(4)	3.881	0.004
Sb(1)	Sb(1)	3.572	0.006
Sb(3)	Sb(3)	2.998	0.022
	Sb(5)	3.280	0.017
Sb(5)	Sb(5)	2.936	0.009

[a] Esd's include only uncertainties in positional parameters.

TABLE I
FINAL ATOMIC PARAMETERS (×10^4) FOR $Yb_{11}Sb_{10}$[a]

Atom	Wycoff notation	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Yb(1)	16n	0	2518 (2)	1886 (1)	38 (1)	22 (1)	6 (0)	0	0	−1 (1)
Yb(2)	8h	1671 (5)	1671 (5)	0	71 (4)	71 (4)	14 (1)	40 (3)	0	0
Yb(3)	4e	0	0	3374 (2)	32 (4)	32 (4)	11 (1)	0	0	0
Yb(4)	16n	0	3364 (2)	3974 (1)	26 (1)	36 (1)	4 (0)	0	0	−1 (1)
Sb(1)	8i	3494 (4)	0	0	26 (3)	45 (3)	5 (1)	0	0	0
Sb(2)	4e	0	0	1283 (3)	23 (5)	23 (5)	8 (2)	0	0	0
Sb(3)	8h	3736 (9)	3736 (9)	0	104 (8)	104 (8)	19 (2)	−1 (5)	0	0
Sb(4)	4d	0	$^1/_2$	$^1/_4$	25 (4)	25 (4)	3 (1)	0	0	0
Sb(5)	16m	2062 (4)	2062 (4)	3245 (2)	35 (2)	35 (2)	8 (1)	6 (2)	−1 (2)	−1 (2)

[a] The esd's × 10^4 are given in parentheses. The form of the thermal ellipsoids is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

The calculated density assuming 4 units of $Yb_{11}Sb_{10}$ per unit cell is 8.6 g/cm³. Density measurements on the spongy material by loss of weight in acetone resulted in a suspiciously low value of 7.6 g/cm³, probably because acetone failed to displace entrapped air. The density was redetermined by immersing the specimen in benzene and evacuating the system so that boiling occurred and benzene vapors could penetrate into the pores to displace the air. When the system was opened to the atmosphere, the vapors condensed to liquid in the pores and additional liquid was sucked in so that a true weight loss was determined. Several such measurements yielded values ranging from 8.11 to 8.24 g/cm³, with an average value of 8.17 (7) g/cm³, considerably closer to the calculated value for the stoichiometry $Yb_{11}Sb_{10}$.

Weissenberg and precession photographs, made with Cu Kα and Mo Kα radiation, respectively, showed that the diffraction symmetry was 4/mmm, that the crystal was mounted along an axis which was labeled b, and that hkl diffraction spectra were present only when $h + k + l = 2n$ with no other systematic absences being

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