Table I. Calculated Energies and Bond Lengths According to the Floating Localized Orbital Model with Spherical Gaussian Functions

Molecules	Negative total energy (hartrees) This work	Negative total energy (hartrees) Hartree–Fock		Bond length, A Calcd	Bond length, A Obsd[h]
H_2	0.956	1.1336[a]		0.780	0.741
LiH	6.572	7.9851[b]		1.712	1.595
Li_2	12.282	14.8718[c]		2.807	2.672
HF	84.635	100.0580[d] (min at R = 0.920 A)		0.779	0.917
BeH_2					
linear	13.214			1.412	
BH_3					
planar D_{3h}	22.297	26.2358[e] (min at R = 1.16 A)		1.245	1.19 (av)
CH_4					
tetrahedral	33.992	39.8660[f] (min at R = 1.10 A)		1.115	1.093
NH_3					
pyramidal C_{3v}	47.568	55.9748[f] (min. at R = 1.04 A)		1.008	1.012
planar D_{3h}	47.141			1.489	...
H_2O					
angular C_{2v}	64.290	75.9224[f] (min at R = 0.963 A)		0.880	0.957
linear	64.203			1.621	...
C_2H_2					
linear, sym	64.684	76.7916[g]	C≡C	1.210	1.205
			C=H	1.073	1.059
C_2H_4					
planar, D_{2h}	65.836	78.0012[g]	C=C	1.350	1.337
			C—H	1.104	1.085

[a] W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32,** 205 (1960). [b] D. D. Ebbing, *J. Chem. Phys.*, **36,** 1361 (1962). [c] P. E. Cade and A. C. Wahl, quoted by G. Das, *ibid.*, **46,** 1568 (1967). [d] E. Clementi, *ibid.*, **36,** 33 (1962). [d] B. D. Joshi, *ibid.*, **46,** 875 (1967). [f] R. Moccia, *ibid.*, **37,** 910 (1962); **40,** 2164, 2176, 2186 (1964). [g] R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *ibid.*, **46,** 2029 (1967). [h] Observed values are taken from L. E. Sutton, Ed., "Interatomic Distances," Special Publication No. 18, The Chemical Society, London, 1965.

The calculated bond lengths are surprisingly close to the experimental values, on the average within 4.4%. Considering the crudeness of the model no such direct quantitative similarity would be expected. However, the model should give general trends which certainly are present.

Bond angles are not as successfully calculated although NH_3 and H_2O are properly predicted to be pyramidal and bent, respectively. The angles are: H-N-H, 88.0° (obsd 106.6°); and H-O-H, 89.5° (obsd 104.5°).

Dipole moments (Debyes) are calculated to be: LiH, 6.56 (obsd 5.882); HF, 1.66 (obsd 1.98); H_2O, 1.92 (obsd 1.84); and NH_3, 1.71 (obsd 1.46).

LiH is a simple example which shows how the orbital parameters behave. One orbital turns out to have a small "radius," ρ, equal to 0.707 bohr and is located 0.0076 bohr from the Li nucleus on the side opposite from the proton. This can be considered an inner-shell Li orbital. The other orbital has a radius of 2.44 bohrs and is located about 89% of the way from Li to H. The bond could therefore be interpreted to be predominantly ionic.

This model has a simpler relation to the original electron pairing and shared pair concepts of Lewis[4] than does the quantum mechanical valence bond method since the present model uses only one orbital per electron pair bond instead of two. It is also related to molecular orbital theory through the use of a single determinantal wave function. Localized molecular orbitals have been discussed particularly by Lennard-Jones and co-workers[5] and by Edmiston and Ruedenberg.[6]

This model constitutes an extension of the Kimball–Neumark[7] spherical Gaussian orbital model which was applied by Neumark to the simple systems He and H_2. The "charge cloud" model of Kimball[7] which conceives of uniformly charged spheres for electron pairs resembles the present model but does not allow for overlap of the spheres and is only pseudo-quantum mechanical. Likewise the tangent-sphere model of Bent[8] and related ideas of King,[9] although giving considerable qualitative insight into molecular structure, are not sufficient for quantitative calculations. Details of the calculations and additional results will be published elsewhere.

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(4) G. N. Lewis, *J. Am. Chem. Soc.*, **38,** 762 (1916); "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, N. Y., 1923.

(5) J. E. Lennard-Jones, *Proc. Roy. Soc.* (London), **A198,** 1, 14 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.*, A202, 155 (1950); J. E. Lennard-Jones and J. A. Pople, *ibid.*, A202, 166 (1950); A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *ibid.*, **A220,** 446 (1953).

(6) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35,** 457 (1963).

(7) Ph.D. Dissertations by G. F. Neumark, L. M. Kleiss, H. R. Westerman, and J. D. Herniter, Columbia University; reviewed by J. R. Platt in "Encyclopedia of Physics," Vol. 37, Part 2, S. Flügge, Ed., Springer-Verlag, Berlin, 1961, p 258.

(8) H. A. Bent, *J. Chem. Educ.*, **40,** 446, 523 (1963); **42,** 302, 348 (1965).

(9) L. C. King, *Chemistry*, 37, 12 (1964).

Arthur A. Frost, Bryant H. Prentice, III, Robert A. Rouse
Department of Chemistry, Northwestern University
Evanston, Illinois

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The Coordination Number of Aluminum(III) in Liquid Ammonia[1]

Sir:

Various nmr techniques[2-4] have been used to determine hydration numbers of ions in aqueous solutions. We have attempted to extend these methods to liquid ammonia and wish to report the results for Al(III) solutions. The method used was to determine the area under the ^{14}N nmr absorption line in the species $Al(NH_3)_x{}^{3+}$ after broadening the solvent line beyond detection by addition of Cu(II). The exchange of bound ammonia in the Cu(II) complex is very rapid.[5] The area measurements were calibrated using various known species.

(1) Report No. RLO-1031-6 of work supported by the U. S. Atomic Energy Commission.

(2) J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **33,** 553 (1960).

(3) R. E. Connick and D. N. Fiat, *ibid.*, **38,** 1349 (1963).

(4) D. N. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88,** 4754 (1966).

(5) J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2,** 478 (1963).

Anhydrous aluminum iodide was prepared by standard methods and dissolved in anhydrous ammonia which was also prepared and handled by standard techniques. The Al(III) concentration was *ca.* 1.35 *M*. In other experiments it had been found that addition of $Cu(NH_3)_4(NO_3)_2$ to the extent of *ca.* 0.2 *M* broadened the solvent ammonia line beyond detection (the bound ammonia line and solvent line occur at essentially the same frequency) and that Cu(II) and I^- were stable in ammonia. Addition of the Cu(II) nitrate salt caused precipitation of some Al(III) the amount of which was determined, and an appropriate correction was made. The ^{14}N nmr absorption line for the bound ammonia (and references) was measured at *ca.* 9300 gauss using equipment previously described.[6] The areas under the curves were measured in various ways and compared with areas obtained for standard aqueous $NaNO_2$, $Co(NH_3)_6{}^{3+}$ in ammonia, $Co(NH_3)_5 \cdot H_2O$ in water, and others. The known solutions gave internally consistent results and were chosen to give line widths and intensities comparable to that found for the Al(III) species. This was done so that all the nmr measurements could be made under essentially identical conditions of radiofrequency level, modulation amplitude, etc. The full width at half-maximum absorption for the bound ammonia line was 1.35 ± 0.14 gauss at 27°. The coordination number of Al(III) was found to be 6.03 ± 0.45 (as an average of four signals).

We were unable to shift the solvent line sufficiently to be useful using either Cu(II) (which produces relatively small shifts) or Co(II) without causing excessively large amounts of broadening. Dysprosium nitrate was found to be too insoluble in ammonia to be useful for shifting the solvent line.

The results imply a relatively long lifetime for the $Al(NH_3)_6{}^{3+}$ species in ammonia consistent with the results of Sutter and Hunt[7] using ^{15}N tracer techniques. A coordination number of six was also found for the hydrated species.[3] The precision of the measurements was limited because of the broad, weak signals involved. Attempts to measure solvation number for Be(II) and Ga(III) have failed so far because of solubility problems. The use of ^{15}N and improved nmr equipment may make it possible to study other species in the future.

(6) H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965).

(7) J. R. Sutter and J. P. Hunt, *J. Am. Chem. Soc.*, **82**, 6420 (1960).

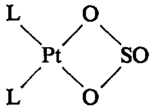
H. H. Glaeser, H. W. Dodgen, J. P. Hunt
Department of Chemistry, Washington State University
Pullman, Washington 99163
Received March 22, 1967

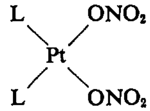
Oxidation of Coordinated Ligands. Sulfato and Nitrato Complexes of Platinum

Sir:

During the recent upsurge in interest in the behavior of d^{10} and d^8 complexes, a variety of working models have been suggested in an attempt to rationalize and predict the chemistry of these species.[1,2] Recently we have inclined strongly to the view that the behavior in solution of the zerovalent complexes $M(PPh_3)_4$ (M = Ni, Pd, Pt) is essentially that of solvated metal atoms. The characteristics[1] of the oxygen and ethylene complexes, $(PPh_3)_2PtO_2$ and $(PPh_3)_2Pt(C_2H_4)$, helped to reinforce this concept and prompted an investigation under homogeneous conditions[3] of those reactions in which platinum has traditionally served as a heterogeneous catalyst; *e.g.*, the contact process.

Passage of SO_2 into a solution of $(PPh_3)_2PtO_2$ at room temperature results in the rapid formation of an air-stable complex which we believe to be the sulfato complex I. *Anal.* Calcd for $C_{36}H_{30}O_4P_2SPt$: C, 53.00; H, 3.68; mol wt, 815. Found: C, 52.92; H, 3.66; mol wt, 795.


I


II

L = PPh_3

The infrared spectrum (Nujol) shows four strong band with some splitting at 1279, 1165 and 1150, 880 and 871, and 650 cm^{-1}, which is in accord with the symmetry of the SO_4 group acting as a bidentate ligand (C_{2v}) and is in reasonable agreement with the spectrum reported by Barraclough and Tobe[4] for the complex $[Co(en)_2SO_4]Br$, one of the few monomeric complexes known to contain bidentate sulfate. The possibility of a sulfur-bonded sulfito complex[5] cannot be ruled out in terms of the number of bands observed, but is, we feel, unlikely in view of the high frequency of the band which we assign to the asymmetric S–O stretch (1279 cm^{-1}). Reaction between SO_2 and a solution of the ethylene adduct, $(PPh_3)_2Pt(C_2H_4)$, results in displacement of ethylene and formation of a brown crystalline complex[6] which loses SO_2 readily on warming (50°) to yield the air-stable, green complex $(PPh_3)_2Pt(SO_2)$. *Anal.* Calcd for $C_{36}H_{30}O_2P_2SPt$: C, 55.17; H, 3.83; S, 4.09. Found: C, 54.92; H, 3.94; S, 4.68. Two strong infrared bands (Nujol) are found at 1182 and 1149 and 1035 cm^{-1}, resulting from asymmetric and symmetric S–O stretching vibrations. The spectrum is strongly indicative of a sulfur-bonded SO_2 adduct, and the complex is presumably of a similar type to $(SO_2)IrCl(CO)(PPh_3)_2$ recently reported by Vaska.[7] Passage of oxygen through a solution of the green SO_2 adduct, or heating the complex in air (110°), results in the formation of the sulfato complex already described.

Similar results are obtained when the oxygen adduct is treated with NO_2, the dinitrato complex (II) being obtained pure and in high yield. *Anal.* Calcd for $C_{36}H_{30}N_2O_6P_2Pt$: C, 51.25; H, 3.56; N, 3.32. Found: C, 51.43; H, 3.65; N, 3.16. The complex

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(1) C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, **3**, 31 (1967).

(2) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966).

(3) It has recently been shown by G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Intern. Ed. Engl.*, **6**, 92 (1967), that a solution of complex $(PPh_3)_2NiO_2$ functions as a catalyst for the oxidation of triphenylphosphine.

(4) C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).

(5) G. Newman and D. B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).

(6) We have learned of closely related experiments by J. J. Levison and S. D. Robinson, *Chem. Commun.*, 198 (1967), following submission of this paper. They report the preparation of the brown, apparently four-coordinated adduct, $(PPh_3)_3PtSO_2$, and its ready oxidation to the sulfato complex, $(PPh_3)_2PtSO_4$, described herein.

(7) L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966).