$FeCH_3$. Separation by this technique is susceptible to additional thermolysis reactions. (2) A sample of the N^+ compound stirred in an acidic melt for 1 day at 40 °C was made basic with 1-BPC addition and quenched with MeOH. The MeOH was carefully removed by vacuum distillation (45 °C, 100 torr) to yield an oily solvolyzed melt, to which H_2O is added. The resultant solution was extracted with Et_2O, and the extracts were dried with K_2CO_3 and these desolvated in vacuo. Comparative TLC (silica gel, 10% CH_2Cl_2 in hexane) suggested that the major volatile product was $C_{10}H_{10}Fe$. Preparative TLC (silica gel, 5% isopropyl alcohol in toluene) gave two mobile bands (R_f = 0.10 and 0.50), only the first of which (0.50) contained ferrocene compounds by ^1H NMR determinations: singlets at 4.25 and 4.19 ppm downfield from Me_4Si (the latter due to $C_{10}H_{10}Fe$). A portion of the unsolvolyzed melt was subjected to ^1H NMR. In addition to the dominant melt components, solute protons at 7.72, 7.61, and 7.49 ppm (apparent multiplet, phenyls) and 4.34, 4.23, 4.18, and 4.11 ppm (apparent multiplet, cyclopentadienyl) downfield of the methyl triplet due to the solvent centered at 0.99 ppm[19] were resolved. (3) A sample of the N^+ compound stirred for 4 days in an acidic melt, reduced with Al wire, and converted to 0.8:1 basic melt was quenched with toluene. The toluene layer was analyzed by ^1H NMR, $^{13}C\{^1H\}$ NMR, and GC–MS; identifiable components were toluene (*m*/*e* 91), $BzNMe_2$ (*m*/*e* 135, 91, 58), $C_{10}H_{10}Fe$ (*m*/*e* 186, 121), $C_{10}H_9FeCH_3$ (*m*/*e* 200, 134, 121), and some $C_{10}H_9FeEt$ (*m*/*e* 214, 199, 134), in which the last three components showed isotropic distribution characteristic of Fe-containing compounds. The ^1H NMR spectrum (benzene-d_6) consisted of a singlet at 4.0 ppm ($C_{10}H_{10}Fe$), a multiplet around 3.97 ppm, and a singlet at 1.84 ppm ($C_{10}H_9FeCH_3$) downfield from Me_4Si. The $^{13}C\{^1H\}$ NMR spectrum showed a cluster of peaks 68–69 ppm downfield from Me_4Si—$C_{10}H_{10}Fe$ at 68.1 ppm and $C_{10}H_9FeCH_3$ at 69.2, 68.7, and 67.4 ppm with methyl at 45.2 ppm. (4) A sample of the N^+ compound stirred in an acidic melt for 4 days was reduced with Al wire and quenched with toluene. The toluene layer was separated into three parts: (a) toluene, (b) volatile solids, and (c) nonvolatile residues. The last two were analyzed by MS and ^1H and $^{13}C\{^1H\}$ NMR. The proton NMR spectrum of the volatile solids consisted of resonances for $C_{10}H_{10}Fe$ (singlet at 4.00 ppm), $C_{10}H_9FeCH_3$ (multiplet at 3.97 and singlet at 1.84 ppm), and some toluene (broad singlet at 7.08 ppm and singlet at 2.11 ppm) downfield from Me_4Si. The $^{13}C\{^1H\}$ NMR spectrum also showed the expected resonances for $C_{10}H_{10}Fe$ (68.1 ppm) and $C_{10}H_9FeCH_3$ (69.2, 68.7, and 67.4 ppm). The MS of the nonvolatile residues showed Fe-containing compounds at *m*/*e* 121 (Fe^+Cp), 134 ($Fe^+C_6H_6$), 186 ($C_{10}H_{10}Fe^+$), and 200 ($C_{10}H_9Fe^+CH_3$). A peak at *m*/*e* 398 corresponding to some dimeric $(C_{10}H_9FeCH_2)_2^+$ also was observed. The ^1H NMR spectrum (benzene-d_6) for the nonvolatile residues showed only one broad resonance in the cyclopentadienyl region (4.0–4.2 ppm) centered at 4.16 ppm. The $^{13}C\{^1H\}$ NMR spectrum indicated only one resonance assignable to ferrocene species at 69.5 ppm downfield from Me_4Si.

It is apparent that attempts to separate the possibly highly reactive radical species from an acidic melt have been an unsuccessful approach to analysis. Although not identifiable by electrochemical methods as the major products in the melt, ferrocene and 1-methylferrocene were frequently encountered products after workup. In situ analyses may be more successful in establishing a definitive structure to the ferrocenium product, if suitable procedures can be found.

Acknowledgment. Support funds were provided by the Solar Energy Research Institute. Assistance in the preparation of this paper by the Chemistry Department, Louisiana State University, is gratefully acknowledged.

Registry No. I, 83527-56-4; II, 83511-13-1; III, 53248-56-9; $C_{10}H_9FeCH_2NMe_3I$, 12086-40-7; $C_{10}H_9FeNMe_2$, 67251-69-8; MeI, 74-88-4; $C_{10}H_9FeCH_2NMe_2$, 1271-86-9; *n*-butyl bromide, 109-65-9.

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[19] Bugle, R., private communication.

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843, and the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Parc Valrose, 06034, Nice Cedex, France

Structure, Bonding, and Chemistry of *closo*-Tetraphosphorus Hexakis(methylimide), $P_4(NCH_3)_6$, and Its Derivatives. 4. Spectroscopic Studies and General Conclusions

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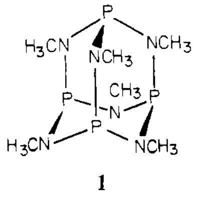
Carbon-13 nuclear magnetic resonance spectra and valence-shell photoionization spectra have been measured for representative compounds of the type $X_nP_4(NMe)_6$ with X = O, S and n = 0–4. The ^{13}C spectra for the series $P_4(NCH_3)_6$, $S_4P_4(NMe)_6$, $O_4P_4(NCH_3)_6$ indicate increasing positive charge on the nitrogen atoms in that order. The PE spectra for the compounds $S_nP_4(NMe)_6$ with n = 0, 1, 3, 4 show a steady increase in the stability of the nitrogen pπ electrons. These results together with previously reported structural data are used to discuss electron distribution in these molecules with particular regard to the extent of P–N π bonding, which is judged to be small but real. The softness and deformability of these molecules appear to be prominent characteristics of closo phosphorus compounds and to provoke various types of disorder; as a consequence, the electron distributions more probably adapt to the geometric structures rather than determining them.

Introduction

Several years ago[2a] we began a program of physical studies of *closo*-tetraphosphorus hexakis(methylimide) (**1**) and some of its derivatives to see whether evidence for a significant amount of N–P pπ→dπ bonding could be obtained. It had initially been our hope that structural data alone would provide strong evidence on this point, and in three earlier papers[2b–4] we have reported structures for **1** and the following derivatives of the type $X_nP_4(NCH_3)_6$: **2**, X = O, n = 4; **3**, X = S, n = 1; **4**, X = S, n = 2; **5**, X = S, n = 3; **6**, X = S, n = 4. For reasons that we shall consider later, the uncertainties in the structural results were much greater than we expected and the structures did not form a basis for unambiguous conclusions about bonding. We have, therefore, also obtained some NMR



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[1] (a) Texas A&M University. (b) Laboratoire de Chimie Minérale Moléculaire.

[2] (a) Cotton, F. A.; Troup, J. M.; Casabianca, F.; Riess, J. G. *Inorg. Chim. Acta* **1974**, *11*, L33. (b) Casabianca, F.; Cotton, F. A.; Riess, J. G.; Rice, C. E.; Stults, B. R. *Inorg. Chem.* **1978**, *17*, 3232.

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[4] Cotton, F. A.; Riess, J. G.; Rice, C. E.; Stults, B. R. *Inorg. Chem.* **1982**, *21*, 3123.

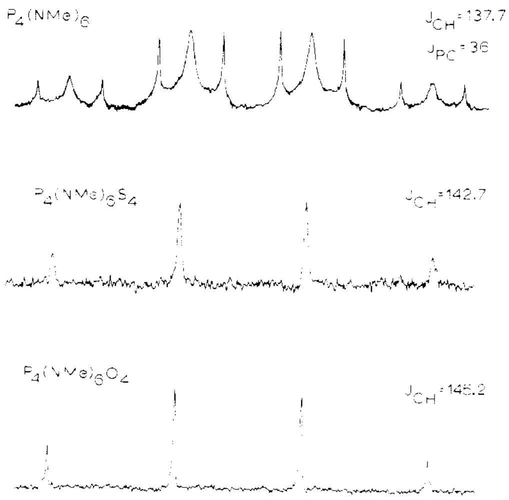

Figure 1. Carbon-13 NMR spectra of the three compounds with T_d symmetry. The chemical shifts are, from top to bottom in ppm downfield from Me_4Si, 89.2, 91.3, and 97.3.

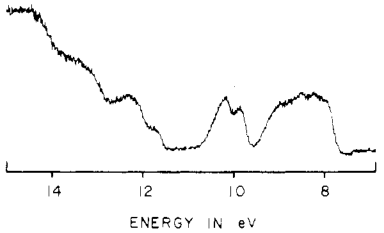

Figure 2. He I photoelectron spectrum of $P_4(NCH_3)_6$ run under conditions of optimum resolution.

data and some photoelectron spectra.

In this paper we report and interpret the new spectroscopic data and present the general conclusions that we feel can be drawn from the totality of the available evidence.

Experimental Section

The compounds were all prepared by methods previously cited.[2-7]

^{13}C NMR Spectra. These spectra were recorded on a JEOL PFT 100/Nicolet 1080 Fourier transform spectrometer at 25.035 MHz. A pulse width of 9 μs, a sweep width of 4000 Hz, and a repetition rate of 2.1 s were employed. Each spectrum shown in Figure 1 is based on 20960 scans. Solutions were prepared with use of benzene that had been thoroughly degassed by repeated freezing and thawing under vacuum and were contained in 10-mm-diameter serum-stoppered NMR tubes. The probe temperature was 22 ± 1 °C.

PE Spectra. These were recorded on a Perkin-Elmer PS 18 spectrometer using He I (21.22 eV) excitation The samples were introduced as solids and were sublimed into the measuring chamber at temperatures of 90–120 °C. The energy scale was calibrated against an internal argon/nitrogen gas mixture. Professor Edgar Heilbronner of the Physikalisch-Chemisches Institut, University of Basel, kindly supplied a pair of He I and He II spectra of $P_4(NCH_3)_6$, recorded under similar instrumental conditions. We are also grateful to Professor R. F. Fenske and Dr. D. L. Lichtenberger for providing the spectrum of $P_4(NCH_3)_6$ shown in Figure 2. We have been unable to achieve comparable resolution with our spectrometer.

Results

NMR Spectra. The ^{13}C spectra of $P_4(NCH_3)_6$, $S_4P_4(NCH_3)_6$, and $O_4P_4(NCH_3)_6$ are shown in Figure 1. Preliminary examination of the spectra of the less symmetrical compounds, **3–5**, indicated that, as expected, they are very complex, and we made no effort to record accurately or interpret these spectra.

Our particular interest was to measure the $^{13}C-^{1}H$ coupling constants in the three compounds with T_d symmetry. As Figure 1 shows, in each case the quartet structure caused by this coupling is well resolved, and the measured values of J_{CH} are given in the figure. It will be seen that for $P_4(NMe)_6$ the effects of $^{31}P-^{13}C$ coupling, with $^2J_{CP} = 36$ Hz, are clearly displayed[8] whereas for $S_4P_4(NCH_3)_6$ there is little and for $O_4P_4(NCH_3)_6$ no evidence of $^{31}P-^{13}C$ coupling. This is in accord with the trend of $^2J_{CP}$ coupling constants in the $(RO)_3P$, $(RO)_3PS$, $(RO)_3PO$ series where R = CH_3, C_2H_5. In these $J_{CP} = +11$ Hz for the first member of each series and about −5 Hz for each of the other members.[9] Presumably in the PN cage compounds there is a similar trend such that for the $S_4P_4(NCH_3)_6$ compound the coupling constant is very close to 0 and for $O_4P_4(NCH_3)_6$ it is almost exactly 0.

Photoelectron Spectra. We begin with the well-resolved spectrum of $P_4(NCH_3)_6$ shown in Figure 2. This spectrum is cleanly divided into three regions: (1) a broad hump, from ~7.9 to ~9.3 V, showing no resolved structure; (2) a doublet, with maxima at 9.88 and 10.20 V, in an intensity ratio of about 1:3; (3) a rising, broadly structured absorption beginning above 11 V.

Region 3 doubtless corresponds to ionization of the various types of P–N, N–C, and C–H σ-bonding electrons. Detailed assignments in this region are not pertinent and need not be attempted.

Absorptions 1 and 2 can be assigned to lone pairs on the nitrogen and phosphorus atoms, respectively. Such an assignment is made by analogy to the assignments made in other aminophosphine molecules such as $P(NMe_2)_3$[10] and is supported by the observation that in a He II spectrum absorption 2 is weaker relative to absorption 1 than in the He I spectrum.

The four phosphorus lone pairs form MO's of symmetry types A and T_2, both essentially nonbonding and not likely to differ much in energy. Hence, the appearance of two closely spaced, relatively narrow peaks, with an approximately 1:3 intensity ratio would be predicted, exactly as observed in region 2.[11] The mean energy, ca. 10 V, is an entirely reasonable one.[10] Finally, in the spectrum recorded with He II excitation, the intensity in region 2 relative to the rest of the spectrum is significantly lower; this sort of intensity dependence is characteristic of phosphorus ionizations.[12]

The absorption in region 1 due to nitrogen atom lone pairs is broad and doubtless consists of two or more overlapping bands. The six pπ orbitals combine under T_d symmetry to form two MO's of symmetries T_1 and T_2; there are also combinations of the empty phosphorus dπ orbitals of T_1 and T_2 symmetries. Thus, all of the six nitrogen lone pairs are permitted, by symmetry, to be engaged in $N(p\pi) \rightarrow P(d\pi)$ bonding interactions. The appearance of the spectrum in region 1 could, then, be due to the fact that there are two orbitals, each with bonding character and each triply degenerate. Ions formed by removal of these electrons would be subject to Jahn–Teller effects, and the Franck–Condon principle would require that there be vibrational excitation accompanying

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(8) The $^2J_{CP}$ value was obtained by trial and error computer simulation of the observed line shape of one member of the quartet. The best fit was obtained with $^2J_{CP} = 36 \pm 1$ Hz and $J_{PP} = 5 \pm 1$ Hz.

(9) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Table 10.47, p 378.

(10) Cowley, A. H.; Goodman, D. W.; Kuebler, N. A.; Sanchez, M.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 854.

(11) For an earlier example of energy splitting due to phosphorus lp–lp interactions, but involving larger energies, cf. the studies on $(PCF_3)_n$ systems by: Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Padolina, M. C. *J. Am. Chem. Soc.* **1974**, *96*, 3666.

(12) Katrib, A.; Debies, T. P.; Colton, R. J.; Lee, T. H.; Rabelais, J. W. *Chem. Phys. Lett.* **1973**, *22*, 196.

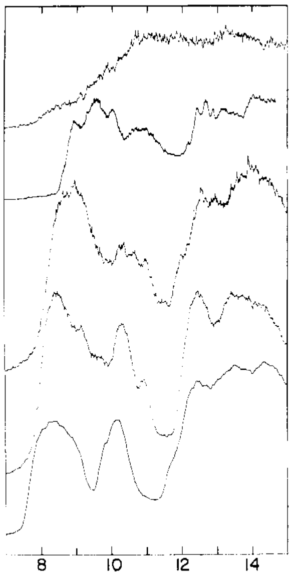

Figure 3. He I photoelectron spectra of, in order from below, $P_4(NCH_3)_6$, $SP_4(NCH_3)_6$, $S_3P_4(NCH_3)_6$, $S_4P_4(NCH_3)_6$, and $O_4P_4(NCH_3)_6$. The abscissa scale is in eV.

ionization. A combination of all these effects can readily account for the type of absorption observed. The broad absorption strongly suggests that the "N pπ" electrons are not simply lone pairs but that they have an appreciable bonding role.

As shown in Figure 3, the introduction of one to four sulfur atoms causes a progressive series of changes in the PE spectra, all of which are consistent with the assignment just discussed for $P_4(NCH_3)_6$.

The effects of introducing one sulfur atom are as follows. First, a peak appears at ca. 10.9 V, which may be assigned to sulfur lone-pair electrons. Second, the absorption due to phosphorus lone pairs is moved slightly (ca. 0.1 V) to higher energy; one might expect two phosphorus lone-pair peaks, due to a_1 and e combinations in C_{3v} symmetry, but there is no clear indication whether or not such a pair of peaks is present. Note that in this series of spectra, the a and t peaks of $P_4(NMe)_6$ were also not resolved. Third, the leading edge of the broad absorption due to nitrogen atom lone pairs, which should now consist of no less than four (a_1, a_2, 2e) peaks, is located at higher energy, by about 0.3 V, and the absorption extends to higher energies so as to overlap significantly with the phosphorus absorption. The center of gravity of the nitrogen absorption appears to have moved by at least 0.4 V to higher energy.

With $S_4P_4(NMe)_6$ we no longer expect a peak from phosphorus atom lone pairs but, instead, a strong absorption due to sulfur lone pairs. Presumably the broad hump with a maximum at about 10.9 V can be so assigned. We can then assign most or all of the structured absorption between ca. 8.6 and 10.3 V to nitrogen atom lone pairs. These have moved markedly (by ca. 1.2 V) to higher energies. This would appear to mean that the N(pπ)–P(dπ) bonding interactions have been considerably strengthened. If it is true that these electrons now have a more strongly bonding role, greater broadening and splitting of the absorption due to vibrational and/or Jahn–Teller effects in the ion are also expected, also in accord with observation.

The spectrum for $S_3P_4(NCH_3)_6$ has characteristics intermediate between those of $SP_4(NMe)_6$ and $S_4P_4(NMe)_6$. The three peaks between 10 and 11 V can presumably be attributed to the remaining phosphorus lone pair and the sulfur lone pairs, but in what order is uncertain. The spectrum of $S_2P_4(NCH_3)_6$ was not reliably obtained since this compound appears to disproportionate under the conditions of measurement.[13]

The structureless appearance of the $O_4P_4(NCH_3)_6$ spectrum is not easy to explain, but it was reproducible. It is, at any rate, not inconsistent with an increase in energy and broadening of the nitrogen lone-pair absorption, the loss of phosphorus lone-pair absorption, and the introduction of oxygen lone-pair ionizations between 10 and 12 V, all of which are to be expected.

Discussion

It is convenient to begin with the NMR data. It was shown some years ago that the $^{13}C-^{1}H$ coupling constants, J_{CH}, in methyl groups vary according to the positive charge of the atom to which the methyl group is bonded.[14] Among the systems that figured prominently in establishing this correlation were methylamines and methylammonium ions. We have examined the compounds $P_4(NCH_3)_6$, $S_4P_4(NCH_3)_6$, and $O_4P_4(NCH_3)_6$ and find that the J_{CH} values are 137.7, 142.7, and 145.2 Hz, respectively. This is consistent with the expectation that, when first sulfur atoms and then oxygen atoms are attached to all of the phosphorus atoms of the P_4N_6 cage, electron density is drawn away from the nitrogen atoms, with oxygen atoms doing this to a greater extent than sulfur atoms.

This result is consistent with increased N(pπ)→P(dπ) bonding in the same order, but this interpretation is not unique. Either a σ mechanism or a π mechanism might explain the increasing charge on the nitrogen atoms, or a combination of both. The increase in the oxidation number of phosphorus upon attachment of the sulfur atom and the further increase in its effective positive charge upon replacement of the sulfur atom by an oxygen atom will cause the phosphorus atoms to attract electron density from the nitrogen atoms, but this may be done through the σ system, through the π system, or both. The NMR observations provide no basis for determining the relative importance of these two pathways.

Turning now to the PE spectra, we see a regular increase in the ionization energy of the nitrogen pπ electrons accompanying the expected degree of electron withdrawal by peripheral sulfur or oxygen atoms. From $P_4(NCH_3)_6$ to $S_4P_4(NCH_3)_6$ the overall shift is about 1 eV. Here again, the observation is consistent with an increase in N(pπ)→P(dπ) bonding, which would stabilize the N p electrons, but it is possible that such a stabilization could also arise indirectly by polarization of the P–N σ bonds so as to cause the more positive nitrogen atoms to bind the π electrons more strongly. It is significant, however, that the well-resolved spectrum of $P_4(NCH_3)_6$ shown in Figure 2 does indicate, by the breadth of the first peak, that the nitrogen pπ electrons are not simply isolated, equivalent lone pairs but that they occupy delocalized molecular orbitals with bonding character. The most reasonable interpretation, though not a required one, is that attachment of S and O atoms to the phosphorus atoms increases the strength of this bonding interaction.

The X-ray structural studies of this class of compounds, although they have not provided as accurate data as initially expected, especially in the details of the structural variations provoked by progressive conversion of the 3-coordinated P(III) to 4-coordinated P(V) atoms, have shown several significant trends throughout the series, all of which are consistent with some N(pπ)→P(dπ) contribution to bonding. These are the closeness to planarity of the bonds about all nitrogen atoms, the significant shortening, by 0.07–0.10 Å, of the P–N bonds with respect to properly redefined P(III)–N(sp^2) and P(V)–N(sp^2) standards, and the shortening of the P(V)–N bond at

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(13) Elkaim, J. C.; Wolff, A.; Riess, J. G. *Phosphorus Relat. Group V Elem.* **1973**, *2*, 249.

(14) Haake, P.; Miller, W. B.; Tysse, D. A. *J. Am. Chem. Soc.* **1964**, *86*, 3577.

the expense of the N-P(III) bond in the P(V)-N-P(III) motif (see detailed discussion in part 3 of this series[4]).

But the one striking general feature revealed by this study is certainly that *all* six compounds investigated showed a surprising and unanticipated degree of disorder. This manifests itself in (1) the lack of precision in the atomic positions resulting in low accuracy of individual bond lengths and angles, (2) a wide spread in bond length for the chemically equivalent bonds of a given molecule, and (3) in some cases gross disorder of an intriguing kind, as with $S_4P_4(NCH_3)_6$, in which one of the sulfur atoms appears to occupy two or even three—depending on temperature—distinct positions in the unit cell.[2b] The polymorphism (orthorhombic or monoclinic, depending on the crystallization procedure) observed for $SP_4(CH_3)_6$[3] is probably related to this tendency to disorder. The wide dispersion in bond length observed in all cases for chemically equivalent bonds was disappointing. Indeed, the presence of 12 equivalent P-N bonds in the molecules having T_d symmetry, i.e., $P_4(NCH_3)_6$, $O_4P_4(NCH_3)_6$, and $S_4P_4(NCH_3)_6$, was expected to lead to very accurate measurements of the P-N bond lengths and was our main incentive for choosing this particular series of molecules, a priori the best suited to our purpose. But in fact the spread of the 24 or 48 crystallographically independent P-N distances (for two or four independent molecules in the unit cells) turned out to be surprisingly wide. The case of $O_4P_4(NCH_3)_6$ is exemplary in this respect: the P-N distances spread from 1.59 to 1.75 Å! with a precision of no better than ±0.02 Å on the mean value 1.667 Å.[2b]

This tendency to disorder thus appears to be a prominent feature of the whole series of closo phosphorimide derivatives and probably, as far as we can judge from the general poor accuracy of hitherto published data on phosphorus oxides and sulfides,[15] a prominent feature of the whole class of closo phosphorus compounds. It can be attributed (1) to their globularity or close-to-spherical nature, which tends to favor rotational disorder and/or a large amplitude of librational motion in crystals and in the extreme cases leads to the existence of a distinct plastic phase, characterized by virtually free rotation, as in $P_4(NCH_3)_6$ or P_4S_{10},[16] and (2) to the fact that there is no central atom tying the atoms together across the cage structure, which therefore can be compared to a soft, deflated tennis ball, subject to easy deformation under the action of crystal packing forces. The molecules reside on crystallographic sites with much less symmetry than the idealized molecules themselves would be expected to have. As a consequence the chemically identical atoms do not experience the same crystal forces, which may thus cause different displacement of individual atoms.

As a result of structural softness, it is probable that it is not the electron distributions that dictate the geometric structures. Instead, the structures easily adapt both to internal constraints, arising from their polycyclic nature, and to external constraints, when in the crystalline form, and the electron distributions then conform to the structures.

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Registry No. 1, 10369-17-2; **2**, 58979-11-6; **3**, 38448-57-6; **5**, 38448-55-4; **6**, 37747-07-2.

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Synthesis, Characterization, and Thermochemistry of Adducts of Zinc, Cadmium, and Mercury Halides with *N*,*N*-Dimethylformamide

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The adducts $ZnX_2{\cdot}n$DMF (X = Cl, Br, I; n = 1, 2), $CdX_2{\cdot}2$DMF (X = Cl, I), $CdX_2{\cdot}$DMF (X = Cl, Br, I), and $HgX_2{\cdot}$DMF (X = Cl, Br) were isolated and characterized by elemental analysis, vibrational spectroscopy, proton magnetic resonance spectroscopy, mass spectrometry, thermal analysis, conductometric measurements, and X-ray diffraction patterns. The shift of the CO stretching vibration to low frequency indicated that DMF is bonded through oxygen to the metals, and on the basis of the data obtained, structures for the adducts are proposed. The standard enthalpies of dissolution of the halides, DMF, and the adducts at 298.15 K, for the reaction $MX_2(s) + n\mathrm{DMF}(l) = MX_2{\cdot}n\mathrm{DMF}(s)$, $\Delta H_R^\ominus$, were as follows (kJ mol^{-1}): $ZnCl_2{\cdot}2$DMF(s), −81.37 ± 0.77; $ZnCl_2{\cdot}$DMF(s), −52.39 ± 0.41; $ZnBr_2{\cdot}2$DMF(s), −90.79 ± 0.48; $ZnBr_2{\cdot}$DMF(s), −53.78 ± 0.57; $ZnI_2{\cdot}2$DMF(s), −86.56 ± 0.74; $ZnI_2{\cdot}$DMF(s), −57.50 ± 0.28; $CdCl_2{\cdot}2$DMF(s), −41.39 ± 0.53; $CdCl_2{\cdot}$DMF(s), −26.84 ± 0.18; $CdBr_2{\cdot}$DMF(s), −35.61 ± 0.36; $CdI_2{\cdot}2$DMF(s), −54.39 ± 0.27; $CdI_2{\cdot}$DMF(s), −30.72 ± 0.18; $HgCl_2{\cdot}$DMF(s), −23.09 ± 0.42; $HgBr_2{\cdot}$DMF(s), −19.02 ± 0.19. From $\Delta H_R^\ominus$, $\Delta H_f^\ominus(MX_2, s)$, and $\Delta H_f^\ominus$(DMF, l) the standard enthalpies of formation were calculated for the same sequence of adducts; viz., $\Delta H_f^\ominus$(s, 298.15 K) = −975.2, −706.9, −898.2, −621.3, −773.3, −504.9, −911.6, −657.7, −591.2, −736.4, −473.3, −486.8, and −429.1 kJ mol^{-1}. The standard enthalpies of the reactions $MX_2{\cdot}n\mathrm{DMF}(s) = MX_2(s) + n\mathrm{DMF}(g)$, $\Delta H_D^\ominus$, and $MX_2(g) + n\mathrm{DMF}(g) = MX_2{\cdot}n\mathrm{DMF}(s)$, $\Delta H_M^\ominus$, were also calculated, and the enthalpy of the metal–oxygen bond was estimated. The calorimetric data suggest that the thermodynamic stability of the adducts decreases from zinc to mercury.

Introduction

N,*N*-Dimethylformamide, the simplest disubstituted amide, has been extensively utilized not only for many laboratory reactions but also in industrial processes as a polymer solvent.[1] Structural features for DMF have been well established by vibrational[2,3] and proton nuclear magnetic resonance[3] spectroscopies. The ^1H NMR spectrum of free DMF shows two

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