for R′ = C_3H_7-*i* and -1.92×10^{-2} K^{-1} for R′ = C_2H_5.

The calculation of absolute values of mean-square amplitudes of vibration is based upon knowledge of one value of f, which is in this treatment derived from a known value of $\langle x^2 \rangle$ obtained from the X-ray data. Since this latter parameter in the X-ray experiment has inherent and undeterminable errors, the calculated values of $\langle x_\perp{}^2 \rangle$ and $\langle x_\parallel{}^2 \rangle$ will propagate this error and are thus quoted only as a guide to the relative changes in the directional amplitudes of motion of the Mössbauer atom. However, the temperature coefficients of these vibrations (i.e., the slopes of the lines in Figures 4 and 5) are independent in this treatment of an absolute value of f and hence the need for $\langle x^2 \rangle$ from the X-ray data. The coefficients are characteristic of the two samples studied and enable comparison of the chelating power of the dithiophosphate ligands. This treatment is capable of extension to other chelating systems, where it can serve to measure the relative binding powers of the ligands without having X-ray data available.

Acknowledgment. Our work is supported by the Office of Naval Research and by the National Science Foundation through Grant CHE-78-26584. We thank M&T Chemicals, Inc., for the donations of organotin starting materials and Professor R. E. Frech of the University of Oklahoma for help with the Raman spectra.

Registry No. $(CH_3)_2Sn[S_2P(OCH_3)_2]_2$, 74096-98-3; $(CH_3)_2Sn[S_2P(OC_2H_5)_2]_2$, 74096-99-4; $(CH_3)_2Sn[S_2P(O\text{-}n\text{-}C_3H_7)_2]_2$, 74097-00-0; $(CH_3)_2Sn[S_2P(O\text{-}i\text{-}C_3H_7)_2]_2$, 74097-01-1; $(C_6H_5)_2Sn[S_2P(OCH_3)_2]_2$, 74097-02-2; $(C_6H_5)_2Sn[S_2P(OC_2H_5)_2]_2$, 74097-03-3; $(C_6H_5)_2Sn[S_2P(O\text{-}n\text{-}C_3H_7)_2]_2$, 74097-04-4; $(C_6H_5)_2Sn[S_2P(O\text{-}i\text{-}C_3H_7)_2]_2$, 73453-95-9; $(C_6H_5)_2Sn[S_2P(O\text{-}n\text{-}C_4H_9)_2]_2$, 74097-05-5; $(C_6H_5)_2Sn[S_2P(O\text{-}i\text{-}C_4H_9)_2]_2$, 74097-06-6; $(C_6H_5)_2Sn[S_2P(OC_6H_5)_2]_2$, 74097-07-7; $(CH_3)_2SnCl_2$, 753-73-1; $(C_6H_5)_2SnCl_2$, 1135-99-5; $(C_6H_5)_2SnO$, 2273-51-0.

Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

Coordination of Adenosine Monophosphate and Inosine Monophosphate to dienPd^{2+} and enPd^{2+} [1]

IMRE SOVAGO[2] and R. BRUCE MARTIN*

Received December 26, 1979

dienPd^{2+} exhibits nearly equal tendencies to react with N(1) and N(7) of AMP. Excess dienPd^{2+} results in formation of a binuclear complex with Pd(II) at both N(1) and N(7). With two available coordination positions, enPd^{2+} reacts with N(1) of one AMP and N(7) of another. Compared to the free ligand at pH 6 downfield shifts occur for the H(8), H(2), and the ribose H(1′) protons. The 0.9-ppm downfield shift for the last proton is unusual. The binding of dienPd^{2+} to inosine is pH dependent, N(7) being favored below pH 5.5 and N(1) above that pH. With both inosine and IMP, excess dienPd^{2+} yields a binuclear complex. With IMP, enPd^{2+} reacts with both N(7) and N(1) to yield at pH 8 chemical shift differences similar to those for the AMP complex. enPd^{2+} induces a base stacked structure in inosine, IMP, GMP, and AMP.

There is a dichotomy in the binding of metal ions to the nucleic base portion of purine nucleosides and nucleotides. Both N(1) in the six-membered ring and N(7) in the imidazole ring of adenosine, inosine, and guanosine serve as donors to metal ions in solution.[3] In the nucleoside monophosphates the pK_a at N(1) is about 3.8 for adenosine, 8.9 for inosine, and 9.4 for guanosine. Thus above pH 5 the relative binding of metal ions to N(1) and N(7) is pH independent for adenosine but remains pH dependent for the 6-oxo nucleosides throughout most of the usual pH scale.[3]

As more reactive counterparts for the antitumor Pt(II) complexes, we have employed Pd(II) complexes which react more readily[4,5] and are not bedeviled by formation in neutral solutions of dihydroxo-bridged dimers which are more inert than mononuclear complexes.[6] With one coordination position available about the tetragonal metal ion, dienPd$(H_2O)^{2+}$ in equimolar solutions favors 5:1 N(1) to N(7) binding to adenosine.[5] When the Pd to adenosine molar ratio reaches 2.0, both N(1) and N(7) sites are occupied in a binuclear complex. The ready accessibility of binuclear complexes suggests the possibility of polymer formation in necessarily *cis*-enPd$(H_2O)_2{}^{2+}$ in its reactions with purine nucleosides. This possibility is explored in this paper.

There has not been agreement on the structures resulting from the reactions of Pd(II) and Pt(II) compounds with guanosine, inosine, and their derivatives. Direct five-membered ring chelation between N(7) and O(6) has been claimed.[7] The evidence, however, for this mode of interaction is not compelling, and alternative interpretations of the results are at least as plausible. For example, rather than being indicative of a strong Pd–O(6) bond,[7] the shift of an inosine band from 1700 to 1625 cm^{-1} may also be interpreted as due to deprotonation at N(1),[8] which is admitted to occur.[7] Once deprotonated, N(1) becomes the most basic site and should bind most metal ions more strongly than N(7).[3] At pH 9.7 two guanosine molecules easily bind via N(1) to the pair of available coordination positions of dmenPd^{2+}.[4] This result indicates that any chelating tendencies in guanosine must be quite weak.

Many complexes with purported N(7),O(6) chelation occur as precipitates.[7] This in itself suggests an alternative structure involving polymer formation via metal ion binding to both N(7) and N(1) of purine bases. Polymer formation has been suggested to occur in neutral solutions of *cis*-$(NH_3)_2Pt^{2+}$ and either inosine[9] or guanosine[10] by means of Raman spectra.

(1) This research was supported by grants from the National Cancer Institute (CA-14832) and from the National Science Foundation.
(2) On leave from the Institute of Inorganic and Analytical Chemistry, L. Kossuth University, Debrecen, Hungary.
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Table I. H(8),H(2) Chemical Shifts of Adenosine, AMP, and Complexes with dienPd^{2+} and enPd^{2+} [a]

		AMP	
free ligand	adenosine[b]	$ROPO_3H^-$	$ROPO_3^{2-}$
BH_1^+		7.35, 7.19	
B	6.99, 6.83	7.23, 6.96	7.32, 6.96
dienPd^{2+}			
BM_1	7.10, 7.38	7.24, 7.35	7.35, 7.35
M_7B	7.61, 7.02	7.80, 7.06	8.04, 7.06
M_7BM_1	7.71, 7.51	7.84, 7.50	8.12, 7.49
enPd^{2+}			
M_7BM_1		8.29, 7.25	

[a] In ppm downfield from *tert*-butyl alcohol internal reference. [b] From ref 5.

Direct chelation between N(7) and O(6) was specifically excluded.

Experimental Section

Nucleosides and nucleotides were obtained from Sigma Chemical Co. Stock solutions of the nitrates of dienPd$(H_2O)^{2+}$ and enPd$(H_2O)_2^{2+}$ were prepared as previously described.[5,6] Potentiometric titrations were performed on a Radiometer titrator usually at a complex concentration of about 5 mM with an ionic strength of 0.2 M adjusted with KNO_3. Proton NMR spectra were recorded on a Varian EM 390 90-MHz spectrometer at a concentration of 30 mM. *tert*-Butyl alcohol was used as an internal reference. Its lack of interaction is indicated by the absence of significant shifts in the en peaks of stacked enPd^{2+} complexes of AMP and IMP shown in the figures. Distinction between the H(8) and H(2) peaks in the proton NMR spectra of purines was often made by observing exchange of H(8) with solvent D_2O when Pd^{2+} is coordinated to N(7).[3]

Results

A solution of AMP at pH 3 contains two acidic protons, the nucleic base proton at N(1) with pK_a = 3.8 and the second phosphate proton to give the dianion with pK_a = 6.2.[3] In a solution containing a 2:1:1 mole ratio of dienPd^{2+} to AMP to OH^-, only the nucleic base proton has undergone deprotonation at a break in the titration curve at pH 4. This solution contains a single binuclear complex with one dienPd^{2+} complexed at N(7) and the other at N(1). The pronounced downfield chemical shifts of the binuclear complex (M_7BM_1) compared to the free ligand (B) are recorded in Table I. The downfield shifts are similar to those previously found for adenosine which are also recorded in Table I.

An equimolar solution of AMP and dienPd^{2+} also titrates 1 equiv of base by pH 4 and a second equivalent by pH 7 with pK_a = 5.9, corresponding to phosphate deprotonation in a ligand with dienPd^{2+} coordinated to the nucleic base. At pH 7 the aromatic region of the NMR spectrum shows two sets of two peaks of about equal intensity assigned to comparable amounts of mononuclear complexes with dienPd^{2+} at N(7) and N(1). The chemical shift assignments appear in Table I under the entries M_7B and BM_1, respectively.

At pH 4, with a singly charged phosphate group on AMP, the aromatic NMR spectrum contains three sets of two peaks that are consistently assigned both with respect to the pH 7 and binuclear complexes just described here and also with the earlier analysis of dienPd^{2+} binding to neutral adenosine.[5] An identical sequence of peaks for both AMP and adenosine is assigned to binuclear and mononuclear complexes with dienPd^{2+} at N(7) and N(1). The chemical shifts for both ligands are tabulated in Table I. For equimolar solutions of both adenosine and AMP the binuclear complex is only about 10% of the total. For the mononuclear complexes of AMP nearly equal amounts of the two species with dienPd^{2+} at N(1) and N(7) are observed. This result contrasts with that observed for adenosine where the N(1)/N(7) mole ratio is 5.[5] Thus addition of mono- or dinegatively charged 5′-phosphate groups to adenosine promotes coordination of dienPd^{2+} at N(7) compared to N(1). An analysis of the coupled effects of phosphate deprotonation and N(1)/N(7) mole ratios in the dienPd^{2+} complex has been made.[11]

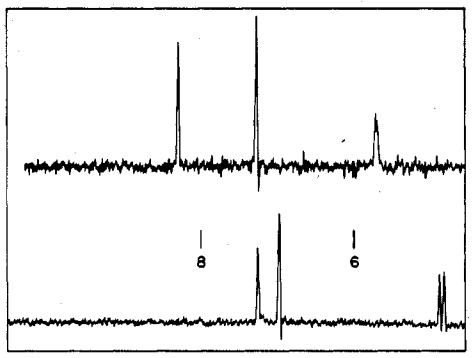

Figure 1. Proton NMR spectrum of enPd^{2+}AMP$^-$ (top) compared to that of free AMP$^-$ at pH 5 (bottom). The vertical lines designate chemical shifts 8.00 and 6.00 ppm downfield from *tert*-butyl alcohol as an internal reference.

Table II. H(8),H(2) Chemical Shifts in Inosine, IMP, and Complexes with dienPd^{2+} and enPd^{2+} [a]

		IMP	
free ligand	inosine	$ROPO_3H^-$	$ROPO_3^{2-}$
B^-	6.87, 6.87		7.20, 6.88
BH_1	7.07, 6.96	7.19, 6.96	7.31, 6.96
dienPd^{2+}			
BM_1	6.95, 6.95		7.17, 6.95
M_7BH_1	7.42, 7.05	7.56, 7.03	7.85, 7.00
M_7BM_1	7.24, 7.03	7.42, 7.03	7.72, 7.01
enPd^{2+}			
M_7BH_1	7.42, 7.01	7.58, 6.95	
M_7BM_1			7.86, 6.70

[a] In ppm downfield from *tert*-butyl alcohol as internal reference.

Unusual results were obtained with equimolar solutions of enPd^{2+} and AMP. In equimolar solutions the nucleic base N(1) deprotonation is complete by pH 3.5 after addition of 1 equiv of base. The NMR spectrum of this solution, containing enPd^{2+}AMP$^-$, compared to that of free AMP$^-$ at pH 5, where the nucleic base is also neutral, is shown in Figure 1. All three complexed peaks in the complex spectrum are shifted downfield compared to those in the free AMP spectrum. In the complexed AMP the chemical shifts of the H(8) and H(2) protons are 8.29 and 7.25 ppm (scale of Table I). By proceeding from left to right in Figure 1 the downfield shifts of the complex compared to the free ligand are 1.06 ppm for H(8), 0.29 ppm for H(2), and 0.9 ppm for the ribose H(1′). Addition of a second equivalent of base to the pH 3.5 solution to deprotonate the phosphate group yields an end point at pH 6. The NMR spectrum of this solution shows only weak peaks, suggesting that the complex of now net zero charge (enPd^{2+}AMP^{2-}) is extensively polymerized. The weak peaks with enPd^{2+} persist into solutions as basic as pH 11 under conditions where an equimolar solution of dienPd^{2+} releases AMP and becomes hydrolyzed to dienPd$(OH^-)^+$.

Inosine, in the pH region considered here, exists in two forms, neutral BH_1 from pH 3 to pH 7 where loss of the proton at N(1) begins to occur with pK_a = 8.7 to give by pH 10 the anion B^- as the major form.[3] The chemical shifts of the H(8) and H(2) protons for both species are tabulated in Table II. Before addition of base, solutions containing 1:2 or 1:1 molar

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(11) P. I. Vestues and R. B. Martin, paper in preparation.

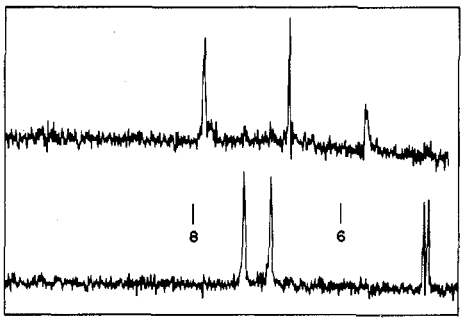

Figure 2. Proton NMR spectrum of $enPd^{2+}IMP^{3-}$ (top) compared to that of free IMP^{2-} at pH 8 (bottom). The vertical lines designate chemical shifts 8.00 and 6.00 ppm downfield from *tert*-butyl alcohol as an internal reference.

ratios of inosine and $dienPd(H_2O)_2^{2+}$ contain predominantly M_7BH_1.

Addition of standard base to a solution containing a 1:2 molar ratio of inosine and $dienPd(H_2O)^{2+}$ produces some M_7BM_1 species even in acid pH; this binuclear complex becomes dominant by pH 9. The binuclear complex is also evident even in equimolar solutions at acid and neutral pH where it occurs with uncomplexed ligand. The mixture of species gives way to BM_1 by pH 6. Inosine in either a 1:1 or 2:1 mole ratio with $enPd(H_2O)_2^{2+}$ yields M_7BM_1 in acid solutions. Addition of base produces precipitates by pH 5, suggesting the presence of a polymer $(-M_1BM_7B-)_n$.

The nucleotide inosine 5′-monophosphate (IMP) undergoes two deprotonations in the pH 4–10 range. The first at $pK_a = 6.2$ corresponds to proton loss from an anionic phosphate group to yield a dianionic phosphate group. The second deprotonation at $pK_a = 8.9$ arises from neutral BH_1 to anionic B^- formation in the nucleic base moiety. In the presence of 1 equiv of $dienPd^{2+}$, the phosphate group deprotonation is acidified by 1 log unit and the nucleic base deprotonation by 2 log units.

With a 2:1 molar ratio of $dienPd^{2+}$ to IMP, two binuclear complexes M_7BM_1 form, one without phosphate deprotonation at pH <5 and the other with the deprotonation at pH >7. The chemical shifts are indicated in Table II. In an equimolar mixture of IMP^- and $dienPd^{2+}$ at pH 3, the species M_7BH_1 occurs almost exclusively. As base is added, phosphate and nucleic base deprotonations occur over a broad pH region becoming complete at pH ~9. From the NMR spectra a mixture of complex species occur throughout this pH range.

Interesting results were obtained with solutions containing $enPd^{2+}$ and IMP^-. Before addition of base at pH <3 an equimolar solution contains predominantly the neutral nucleic base with Pd at N(7), M_7BH_1 with the chemical shifts given in Table II. In equimolar solutions with $enPd^{2+}$ both IMP^- and GMP^- titrate 2 equiv of base by pH 8. The second equivalent corresponds predominantly to the phosphate deprotonation from the complex with $pK_a \approx 5.5$. The first equivalent reflects mainly a pronounced lowering of NH_1 deprotonation from $pK_a \approx 9$ in the free ligands to the pH 3–4 region in the complexes. After titration of these two protons the soluble complex at pH 8 corresponds to net negatively charged $enPd^{2+}IMP^{3-}$. The NMR spectrum of this pH 8 complex is compared to that of the free ligand at the same pH in Figure 2. For the complex H(8) is shifted 0.55 ppm to lower field, H(2) is shifted 0.26 ppm to higher field, and the ribose H(1′) proton is shifted 0.8 ppm to lower field. Other ribose peaks also move downfield into the HDO peak.

Similar chemical shift changes occur in identical experiments with deoxyinosine monophosphate. Compared to the unbound ligand at pH 7 the complex at pH 8 displays for H(8) a 0.63-ppm downfield shift, for H(2) a 0.24-ppm upfield shift, and for the H(1′) ribose proton a 0.6-ppm downfield shift. In the case of the deoxyinosine monophosphate complex, however, both aromatic protons appear as doublets separated by 0.08 ppm. Similar experiments conducted with $enPd^{2+}$ and GMP gave weak spectra with opalescence and precipitation in some solutions. Slight opalescence also appeared in acidic solutions with IMP.

Discussion

Interpretations of chemical shifts in the NMR spectra are suggested only after close correlation with potentiometric titration results of similarly composed solutions. Consistent patterns of protonation and metalation shifts of both H(2) and H(8) protons are evident by comparing chemical shifts in Tables I and II. Furthermore the shifts observed for $dienPd^{2+}$ and AMP closely parallel those already deduced for adenosine.[5] Some unusual shifts have already been noted in the Results, and these systems will be the main subject of this section. First, however, we note the pH dependence of $dienPd^{2+}$ binding to inosine.

The results for equimolar mixtures of inosine and $dienPd^{2+}$ indicate coordination at N(7) at low pH to give the complex M_7BH_1. The N(1)H proton is lost by pH 9 where almost exclusively the ligand binds $dienPd^{2+}$ at N(1). The midpoint of this transfer from N(7) to N(1) of $dienPd^{2+}$ binding to inosine occurs at pH ~5.5. For CH_3Hg^+ and inosine the crossover occurs at pH 4.3.[3,12]

In the pH 4–6 region equimolar solutions of inosine and $dienPd^{2+}$ also contain, even as the predominant species, quantities of the binuclear M_7BM_1 complex. The presence of the binuclear complex of dienPd and inosine even in 1:1 mixtures is reminiscent of the early finding that CH_3Hg^+ also exhibits a pronounced tendency to form binuclear complexes with inosine.[12] Thus it appears to be a property of the ligand inosine rather than the metal ion that produces the tendency to favor 2:1 over 1:1 complexes.

The pronounced chemical shifts observed in equimolar solutions of either AMP or IMP and $enPd^{2+}$ (Figures 1 and 2) suggest stacking interactions. With two ligand donor atoms at N(1) and N(7) and two cis coordination positions available in $enPd^{2+}$, each ligand is bound to two different Pd and each Pd to two different AMP ligands. It is informative to use the binuclear complexes of $dienPd^{2+}$, where metal ion induced stacking does not occur, as the base line for evaluating the chemical shifts in the M_7BM_1 complexes of $enPd^{2+}$.

With respect to the binuclear complex of $dienPd^{2+}$ and AMP, M_7BM_1, where both N(7) and N(1) are coordinated, the equimolar $enPd^{2+}$ and AMP complex at pH 3.5 shows a 0.45-ppm downfield shift of H(8), a 0.25-ppm upfield shift of H(2), and a 0.8-ppm downfield shift of the ribose H(1′) proton. After phosphate deprotonation to yield an overall neutral complex at pH 6, the NMR spectrum becomes broad and ill-defined, suggesting an extensively stacked polymer.

Compared to the binuclear M_7BM_1 complex of IMP and $dienPd^{2+}$, in the $enPd^{2+}$ complex with a dinegative phosphate chemical shifts are 0.14-ppm downfield for H(8), 0.31-ppm upfield for H(2), and most notably 0.8-ppm downfield for the ribose H(1′). Except for a smaller downfield shift for H(8) these shifts are similar to those made in the comparison of AMP complexes.

The 0.8-ppm downfield shift of the ribose H(1′) proton in both AMP and IMP complexes of $enPd^{2+}$ is unusual. The directions of the shifts suggest that in a stacked structure the H(2) proton lies in the shielding cone of another purine ring while the H(8) and H(1′) protons lie outside of the shielding cone. The sharp NMR spectrum in Figures 1 and 2 suggest that the stacks are short. After phosphate deprotonation the

(12) R. B. Simpson, *J. Am. Chem. Soc.*, **86**, 2059 (1964).

AMP complex becomes of zero net charge and the NMR spectrum becomes broad, suggesting long stacks.

There is a significant contrast between the equimolar $enPd^{2+}$ complexes of AMP and those of IMP or GMP. The $(enPd^{2+}AMP^{2-})^0$ complex at pH 6 contains a dinegative phosphate group. Addition of a proton to yield a uninegative phosphate at pH 3.5 yields shorter stacks, the NMR spectrum of which appears in Figure 1. The NMR spectrum in Figure 2 corresponds at pH 8 to short stacks of $(edPd^{2+}IMP^{3-})^-$, which contains in addition to a dinegative phosphate a negative charge on the nucleic base due to deprotonation at N(1). The complex of net zero charge appears at pH 5 and is produced by adding a proton mainly to the phosphate group. This addition makes it of a single negative charge while there also remains a negative charge on the nucleic base. Thus the charge distribution differs in the two overall neutral complexes of $enPd^{2+}$. The AMP^{2-} complex at pH 6 contains a dinegative phosphate while the IMP^{2-} complex at pH 5 contains a uninegative phosphate and a negatively charged purine base.

In reference to the introduction section, not one item of information garnered in this research demands or even suggests the presence of N(7)–O(6) chelation in oxopurines or N(7)–N(6) chelation in adenine derivatives. On the contrary, this investigation has confirmed once again that a deprotonated N(1) site in a purine is a metal binding site. With two or more coordination positions available on a metal ion, the availability of both N(7) and N(1) purine sites leads easily to polymer formation, which is extensive in complexes of net zero charge.

Acknowledgment. We are grateful to Dr. Per Ivar Vestues for discussions concerning this research.

Note Added in Proof. Recent work by Dr. P. I. Vestues in this laboratory indicates significant hypochromic effects in ultraviolet absorption spectra and enhanced circular dichroism magnitudes in solutions where polymer formation is proposed in this paper.

Registry No. AMP, 61-19-8; IMP, 131-99-7; Pd, 7440-05-3.

Contribution from the Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

Metal–Metal Interactions in One Dimension. 2.[1] Electronic Structure of Palladium(II) Dithioacetates

G. CIULLO and O. PIOVESANA*

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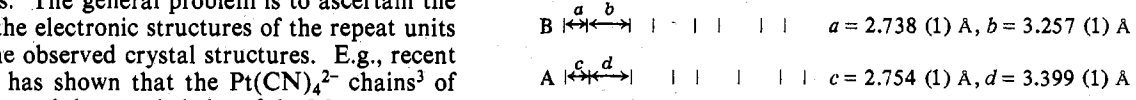
The electronic structures of the monomeric $Pd(CH_3CSS)_2$ and dimeric $Pd_2(CH_3CSS)_4$ molecules have been investigated by using an approximate, parameter-free LCAO–MO–SCF method. The total energy of PdL_2 is found to be almost exactly half that of Pd_2L_4, in agreement with the coexistence of the two molecules in solution. Calculated excitation energies are in good agreement with experimental optical data. The Pd–Pd interactions in the dimer are of bonding type and are interpreted as mainly due to the metal $4d_{z^2}$ and $5p_z$ orbitals. The possible role of intermolecular Pd–Pd interactions in determining the one-dimensional solid-state arrangements of PdL_2 and Pd_2L_4 is discussed.

Introduction

The highly anisotropic properties of one-dimensional inorganic systems are assumed in general to be due to one-dimensional d_{z^2} bands lying at the Fermi level.[2] This implies, in general, structures built up by planar molecules stacking, as closely as possible, along the normal to their planes.[2] A point of crucial importance in the design of such new materials, and which is still matter of controversy, is whether the M–M interactions can be responsible for the adoption of the desired columnar structure or whether the structure is favored by lattice energy considerations and its natural adoption permits these interactions. The general problem is to ascertain the extent to which the electronic structures of the repeat units can determine the observed crystal structures. E.g., recent theoretical work has shown that the $Pt(CN)_4^{2-}$ chains[3] of $K_2Pt(CN)_4(H_2O)_3$ and the metal chains of the Magnus green salt[4] are antibonding and essentially nonbonding, respectively. The main reason appears to be that, contrary to previous assumptions, the mainly d_{z^2} orbitals on the isolated units of these compounds lie well below[4,5] the highest occupied energy level, and appreciable solid-state interactions and/or partial oxidation must occur in order to have bound states and to raise the d_{z^2} band up to the Fermi level.[3,4]

In the preceding paper[1] we described the preparation, constitution, and structure of the dithioacetic acid derivatives of palladium(II). The X-ray structures of two phases, based on a common 2:1 ligand to metal ratio, involve linear chains of directly interacting metal atoms, with short M–M contacts, as a result of a one-dimensional arrangement of either dimeric (structure B) or alternating monomeric and dimeric units[6] (structure A), i.e.



These structural patterns are of interest in light of the empirical fact that the vast majority of the d^8 complexes involving 1,1- or 1,2-dithiolato ligands adopt essentially monomeric, often laterally displaced structures which do not allow short M–M contacts.[7] It is of further interest that the rather unique

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(6) The monomeric molecule has been assumed to be planar (the maximum deviation from the least-squares plane is 0.02 Å). The dimer involves four bridging ligands. The distance between the S_4 planes is 0.14 Å longer than the Pd–Pd distance. The two parallel S_4 squares are rotated in a tetragonal twist from the eclipsed D_{4h} structure by 22.5° in form A and 25° in form B. Other structural parameters are in ref 1.
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