at this pressure but instead gradually rises with increasing pressure throughout the pressure range studied.

For an intrinsic, wide-band semiconductor σ_0 is directly proportional to the sum of the "hole" and "electron" mobilities, and to the extent that the effective masses of these carriers are independent of pressure, its variation with pressure can provide information regarding the dependence of these mobilities upon the internuclear distances in the solid.[23] Under these conditions the character of the $\ln \sigma_0$ *vs.* pressure curve for MGS may be explained in terms of a gradual but continuous increase in the mobilities of the carriers in this complex with increasing pressure. This conclusion is consistent with the current band model for the electronic structure of MGS,[2,4a] in that the increased platinum orbital overlaps that would be anticipated from the observed decrease in metal–metal distances with pressure should lead to wider "d_{z^2}" and "p_z" bands and therefore higher mobilities. In this context the ΔE pressure dependence and thereby the maximum in the conductivity *vs.* pressure curve for MGS presumably reflects changes in the d_{z^2}–p_z band gap occurring under pressure and consequently contains information regarding the dependence of this band gap upon the internuclear distances in the solid.

The decrease in this band gap with increasing pressure can be readily understood in terms of the increase in band widths with decreasing metal–metal distance. On the other hand, the interpretation of the decrease in conductivity observed at very high pressures for both MGS and $Ir(CO)_2(acac)$ in terms of band gap changes obviously requires consideration of internuclear distance changes other than of the intermetallic type.

A similar reversal in the conductivity *vs.* pressure curve has been observed previously for ferrocene and was explained on the basis of electronic structure changes occurring within the ferrocene molecules caused by a decrease in the intramolecular distances.[24] The results of our high-pressure spectral studies have already shown that such intramolecular distance changes can also be important in determining the physical properties of the d^8 metal complexes under pressure. On the basis of these results and the molecular orbital calculations on MGS to be discussed in the following paper,[6] it appears likely that such intramolecular effects are indeed responsible for the conductivity behavior observed for MGS and $Ir(CO)_2(acac)$ at very high pressures.

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Studies of Intermolecular Interactions in Square-Planar d^8 Metal Complexes. II. A Molecular Orbital Study of Magnus' Green Salt

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The intermolecular interactions in Magnus' green salt (MGS) and their dependence upon some of the important structural parameters in the solid are explored using semiempirical molecular orbital theory and elementary band structure calculations. These studies indicate quite significant intermolecular effects at internuclear distance values appropriate to MGS, yet no significant covalent bonding between the platinum atoms in this structure. The substantial dependence of the electronic structure upon both the inter- and intramolecular distances in MGS evidenced by these calculations is discussed in light of the available experimental information on this and related square-planar d^8 metal complexes.

Introduction

In the preceding paper[1] the results of high-pressure physical measurements on Magnus' green salt, $Pt(NH_3)_4PtCl_4$ (MGS), and other d^8 metal complexes which exhibit columnar stacking in the solid state were interpreted in terms of pressure-induced internuclear distance changes. In order properly to evaluate these results in terms of the electronic structure changes occurring in these solids under pressure and, thereby, to obtain a better understanding of the structure–property relationships in this type of compound, a molecular orbital study of MGS was undertaken using the extended Hückel approach. The results of this study and of a simple band theory calculation carried out on MGS are described in this paper.

Because of the approximate nature of these calculations it is important to realize that the quantitative aspects of the results obtained cannot be taken too literally. However, we believe that these results do provide a reasonably accurate qualitative picture of the intermolecular interactions in MGS and the manner in which these interactions depend upon the important structural parameters in the solid.

Previous theoretical work on complexes of this type have been limited largely to qualitative applications of molecular orbital and elementary band theory involving no numerical computations. The first such application of molecular orbital theory in 1957 led to the suggestion that significant intermetallic bonding could occur within the linear chains of metal atoms in these structures, due to overlap of the filled d_{z^2}-like and empty p_z-like orbitals

[1] L. V. Interrante and F. P. Bundy, *Inorg. Chem.*, **10**, 1169 (1971).

on these metals.[2] It was suggested further that such bonding may be effective in stabilizing the columnar stacking exhibited by these complexes and in determining their physical properties. Frequent reference to such polymeric metal–metal bonding and its presumed relationship to physical properties has appeared in subsequent work on these materials.[3]

A semiquantitative molecular orbital study of one such complex, nickel dimethylglyoxime, revealed no significant bonding interaction between the metal atoms in this case; however, it was suggested that the interaction of b_{1u} (p_z-like) molecular orbitals may give rise to a crystal band of significant width which could play an important role in determining the unusual spectral properties of this complex in the solid state.[4] This concept was later extended to MGS by Miller,[5] who derived the general form of the p_z- and d_{z^2}-like bands from elementary band theory. On the basis of this band model, it was anticipated that significant electrical conductivity might be observed in MGS along the chain direction. The subsequent verification of such properties in MGS and several other complexes of this type, as well as the apparent agreement obtained in the case of MGS between the thermal activation energy for conductivity, the photoconductivity response curve, and the position of a near-infrared transition,[6] have led to the extensive use of this hypothesis in accounting for the results of experimental work in this area.[3,6,7]

Method of Calculation

MO Calculations.—The extended Hückel theory,[8] an approximate LCAO–MO technique, has been employed in this study. A self-consistent determination of charge to within 0.02 electron is made by adopting a procedure for obtaining certain matrix elements developed by Cotton and Harris[9] in their study of $PtCl_4^{2-}$ and also used by Zumdahl and Drago.[10] The charges and bond orders were obtained by using a Mulliken population analysis.[11]

Matrix Elements.—The diagonal matrix elements of the Hamiltonian (H_{ii}) for Pt and Cl have been taken as $H_{ii} = -(\mathrm{VSIP})_i$, where the VSIP's (valence state ionization potentials) are those used by Cotton and Harris. Their charge correction of 1 eV/unit charge increment to the VSIP's was also employed. The diagonal matrix element for H^0 was taken as -13.60 eV and the values for N^0 were taken as -26.79 and -14.61 eV which are averages of the two lowest term values for the 2s and 2p orbitals, respectively.[12] The variation of these values as a function of the incremental change in charge was taken as 0 eV/unit charge for H and 1 eV/unit charge for N. These values were chosen on the basis of simplicity after various proportionality relations between charge and the VSIP, ranging from 0 to 5 eV/unit charge in the case of H and 0 to 3 eV/unit charge for N, and the quadratic dependence of Basch, *et al.*,[12] had been investigated. These methods all gave qualitatively the same results for the $Pt(NH_3)_4^{2+}$ ion and platinum-based MO energy levels which were within 0.1 eV of the values quoted herein.

The off-diagonal matrix elements of the Hamiltonian were approximated by the usual Mulliken–Wolfsberg–Helmholz approximation $H_{ij} \approx K(H_{ii} + H_{jj})S_{ij}/2$ with K set equal to 1.8.

Atomic Orbitals.—The atomic orbitals chosen for Pt and Cl were identical with those employed by Cotton and Harris and the H atom was represented by a 1s Slater function with an exponent of 1.0. For the nitrogen 2s and 2p orbitals a single Slater function of the appropriate type was used with orbital exponents chosen best to approximate overlaps between self-consistent field (SCF) functions, using a procedure similar to that employed by Cotton and Harris in their determination of the orbital exponents for Pt and Cl.[9] This involved (a) calculation of the overlaps among the Pt 6s, 6p, and 5d (σ, π, δ) Slater functions and SCF functions on nitrogen[13] at the Pt–N distance found in MGS, (b) replacing the nitrogen SCF functions by Slater orbitals whose exponents were varied until the calculated overlaps agreed with those obtained in (a), and (c) weighting the exponents obtained in (b) for each type of overlap by the value of that overlap and then averaging. This procedure gave the values 1.934 and 1.746 for the 2s and 2p exponents, respectively. A separate series of calculations showed that these exponents were in the same range as those which optimized the agreement with the spectrum. These values were used throughout the calculations, with no changes made as the charge distribution changed in converging to self-consistency.

Atomic Coordinates.—For the NH_3 group the bond angle and internuclear distances appropriate to ammonia were assumed. The other internuclear separations and bond angles were obtained from the results of a single-crystal X-ray study of MGS.[14] The configuration of $Pt(NH_3)_4^{2+}$ assumed in the calculation is shown in Figure 1, and the geometric relationship of the $PtCl_4^{2-}$ group to the $Pt(NH_3)_4^{2+}$ group is shown in Figure 2.

Band Structure Calculations.—A one-dimensional tight-binding calculation employing four bands (two d_{z^2} and two p_z) was carried out on a hypothetical linear chain of platinum atoms.[15] The calculations were performed only at $k = 0$ and $k = \pi/2a$, where a is the repeat distance.

The matrix elements in this calculation were determined by taking appropriate linear combinations of the matrix elements from the MO calculations.[15] The VSIP's were obtained from the results of the MO calculations on the free ions $Pt(NH_3)_4^{2+}$ and $PtCl_4^{2-}$, and only nearest neighbor overlaps were considered (*i.e.*,

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[3] (a) L. K. Monteith, L. F. Ballard, and C. G. Pitt, *Solid State Commun.*, **6**, 301 (1968); (b) C. N. R. Rao and S. N. Bhat, *Inorg. Nucl. Chem. Lett.*, **5**, 531 (1969); (c) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969); (d) T. W. Thomas and A. E. Underhill, *Chem. Commun.*, 725 (1969).

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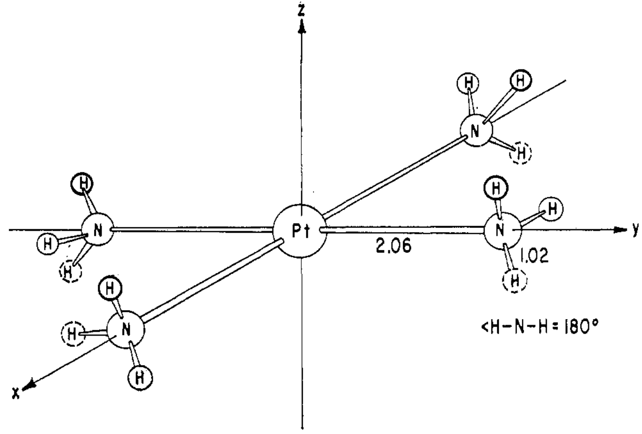

Figure 1.—The coordinate system and molecular configuration used in the MO calculations on $Pt(NH_3)_4^{2+}$: O, atoms centered on the *xy* plane; **O**, atoms above this plane; ◌, atoms below the plane.

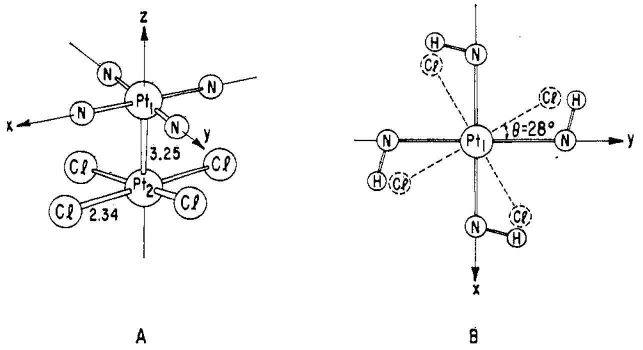

Figure 2.—The coordinate system and molecular configuration used in the MO calculations on $Pt(NH_3)_4PtCl_4$: A, a perspective view excluding all H atoms; B, a view parallel to the metal–metal (*z*) axis showing only those H atoms at $z = 0$; O, atoms centered on the *xy* plane; ◌, atoms below the *xy* plane.

$S_{ij} = 0$ for $j \neq i + 1$). These overlaps were calculated using the same Slater atomic orbitals employed in the MO study.

The effect of changes in the intra- and interionic distances in MGS upon the band structure was determined, in the former case, by using H_{ii} values obtained in MO calculations on the free ions at reduced internuclear distances and, in the latter, by changing the chain repeat distance, *a*.

Results and Discussion

Molecular orbital calculations were carried out on the constituent ions of MGS, $Pt(NH_3)_4^{2+}$ and $PtCl_4^{2-}$, and on combinations of these ions up to $[Pt(NH_3)_4PtCl_4]_2$ arranged in the stacking configuration found for MGS by X-ray crystallography (Figure 2). Also, as the main objective of this study was to correlate the results of high-pressure physical measurements on MGS with possible structural changes occurring in the solid under pressure, the effect of changes in the internuclear distances and the angle between the Pt(1)–N and Pt(2)–Cl bond directions in the $(Pt(1))(NH_3)_4(Pt(2))Cl_4$ unit (Figure 2) were also investigated.

The results of the calculations on $Pt(NH_3)_4^{2+}$ and $PtCl_4^{2-}$ are presented in Table I and Figure 3. Except for a slight increase in the Pt–Cl distance (2.33 to 2.34 Å) to conform to the value found for this ion in MGS, the $PtCl_4^{2-}$ calculation was essentially identical with that previously reported by Cotton and Harris.[9] The close agreement between the results obtained here and those of Cotton and Harris provides a good check on both calculations.

The results obtained for $Pt(NH_3)_4^{2+}$ and their rela-

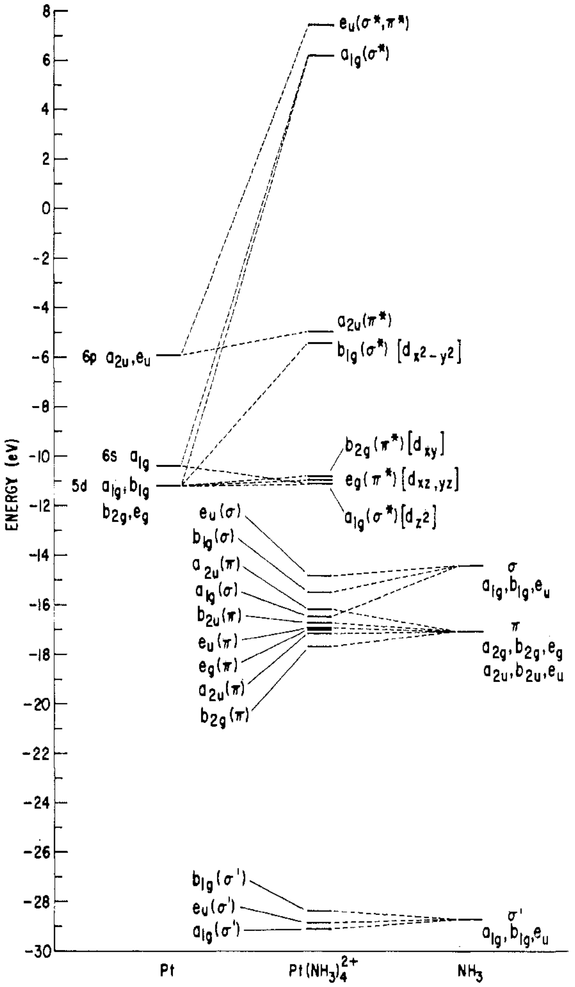

Figure 3.—A partial one-electron MO energy level diagram for $Pt(NH_3)_4^{2+}$; only the principal correlation lines are shown. The energy levels for NH_3 were derived from a separate MO calculation carried out on that molecule using the same input parameters (H_{ii}'s, α_i's, etc.) as in the $Pt(NH_3)_4^{2+}$ calculation.

TABLE I

A PARTIAL LIST OF ONE-ELECTRON MO EIGENVALUES FOR $Pt(NH_3)_4^{2+}$ AND $PtCl_4^{2-}$

$PtCl_4^{2-}$			$Pt(NH_3)_4^{2+}$		
MO	Energy, eV	Symmetry label[a]	MO	Energy, eV	Symmetry label[a,b]
1, 2	8.08	$e_u(\sigma^*, \tau^*)$	13, 14	7.50	$e_u(\sigma^*, \pi^*)$
3	3.81	$a_{1g}(\sigma^*)$	15	6.21	$a_{1g}(\sigma^*)$
4	−4.74	$a_{2u}(\pi^*)$ [$6p_z$]	16	−4.92	$a_{2u}(\pi^*)$ [$6p_z$]
5	−6.91	$b_{1g}(\sigma^*)$ [$5d_{x^2-y^2}$]	17	−5.39	$b_{1g}(\sigma^*)$ [$5d_{x^2-y^2}$]
6	−10.53	$b_{2g}(\pi^*)$ [$5d_{xy}$]	18	−10.78	$b_{2g}(\pi^*)$ [$5d_{xy}$]
7, 8	−10.71	$e_g(\pi^*)$ [$5d_{xz,yz}$]	19, 20	−10.92	$e_g(\pi\ )$ [$5d_{xz,yz}$]
9	−10.99	$a_{1g}(\sigma\ )$ [$5d_{z^2}$]	21	−11.07	$a_{1g}(\sigma^*)$ [$5d_{z^2}$]
10	−13.59	$a_{2g}(\pi)$	22, 23	−14.81	$e_u(\sigma)$
11, 12	−13.92	$e_u(\pi, \sigma)$	24	−15.47	$b_{1g}(\sigma)$
Total energy = −627.60 eV			Total energy = −711.81 eV		

[a] D_{4h} symmetry labels are used with the bonding or antibonding character of the MO and the symmetry with respect to the M–L bond axes indicated in parentheses (*cf.* ref 16). The MO's which are primarily metal p_z or d in character are further identified by means of the appropriate atomic orbital in brackets. [b] The use of D_{4h} symmetry labels is maintained here to permit direct comparison with the $PtCl_4^{2-}$ case, although these are not strictly appropriate to the model used in the calculation.

tionship to the $PtCl_4^{2-}$ case are entirely consistent with both chemical intuition and the available experimental information on these complexes. For instance, the significantly larger b_{1g} ($d_{x^2-y^2}$)–b_{2g} (d_{xy}) orbital separation observed for $Pt(NH_3)_4^{2+}$ as compared to $PtCl_4^{2-}$ is consistent with the positions of Cl^- and NH_3 in the spectrochemical series and reflects the acknowledged differences in the σ- and π-donor–acceptor properties of these ligands.[16] Also the order of the "d-like" MO energy levels remains, $d_{x^2-y^2} > d_{xy} > d_{xz,yz} > d_{z^2}$, in good agreement with the results of spectral studies on the $Pt(NH_3)_{4-n}Cl_n^{2-n}$ ($n = 0$–4) complexes.[16,17] Finally, the charge on the platinum in $Pt(NH_3)_4^{2+}$ obtained from this calculation (0.56+) is significantly higher than that obtained in the $PtCl_4^{2-}$ case (0.44+), as would be expected on the basis of the relative electron affinities of Cl^- and NH_3.

The effect, when combining these two ions in the manner illustrated in Figure 2, upon the energies of the 5d- and $6p_z$-like molecular orbitals is shown in Figure 4.

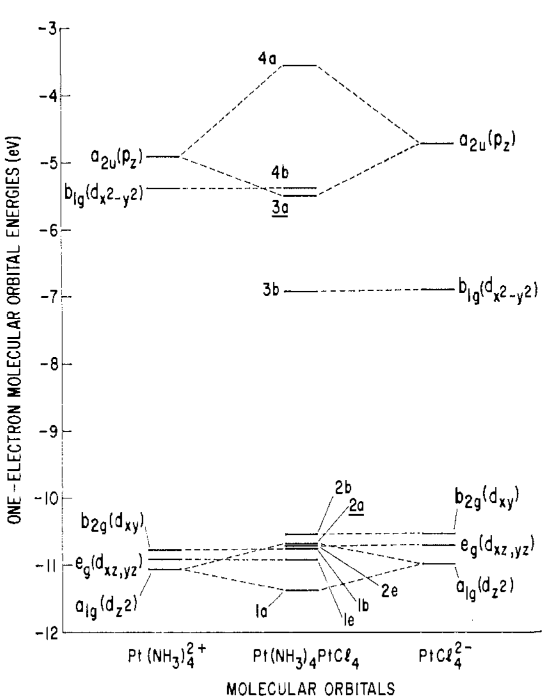

Figure 4.—A partial one-electron MO energy level diagram for $Pt(NH_3)_4PtCl_4$ and its constituent ions.

The order of energy levels follows that obtained for the individual ions, with the mainly $PtCl_4^{2-}$-based 2b and 3b MO's remaining the highest occupied and lowest unoccupied levels, respectively, in the ion pair. Indeed, of the MO's in Figure 4, the only ones with energies significantly different from those of their counterparts in the individual ions are the four "a" levels, which consist largely of p_z and d_{z^2} platinum atomic orbitals.[18]

Further information regarding the interaction between the platinum atoms in this structure was obtained by means of a Mulliken population analysis[11] of the calculated MO's. This analysis provides a measure of the electron density in the bonding region between two atomic orbitals which, when summed for all atomic orbitals on a given pair of atoms over all occupied MO's, gives the reduced overlap population or "covalent bond order" between those atoms. The results of such an analysis on $Pt(NH_3)_4PtCl_4$ indicates a net Pt–Pt bond order of 0.039 of which 0.038 is due to σ-bond interactions (mostly of the p_z–d_{z^2} type but also some s–p_z) and 0.001 comes from π-bond interactions involving the $p_{x,y}$ and $d_{xz,yz}$ orbitals on the Pt atoms. Especially when viewed in the light of the 0.37 and 0.40 values derived for the Pt–N and Pt–Cl bond orders, respectively, and the fact that some of the ligand–ligand antibonding interactions in this ion pair approach –0.01, the net Pt–Pt bond order derived here is not very suggestive of appreciable metal–metal bonding in MGS.

As was pointed out previously[19] a rough estimate of the metal–metal bond energy in binuclear complexes of this type can be obtained by considering the change in energy of the occupied, predominantly metallic molecular orbitals which occurs upon combining the mononuclear "halves" of the complex. In the case of $Pt(NH_3)_4PtCl_4$ this energy is given by the relation

$$\text{Pt–Pt bond energy} \approx \sum_i N(i)\epsilon_i[Pt(NH_3)_4^{2+}] + N(i)\epsilon_i[PtCl_4^{2-}] - N(i)\epsilon_i[Pt(NH_3)_4PtCl_4]$$

where $N(i)$ is the number of electrons in the molecular orbital, ϵ_i is the energy of that molecular orbital, and the sum is over all metal-like molecular orbitals.[20] This yields a net Pt–Pt bond energy of *ca.* 0.2 kcal/mol, indicating that, even considering the approximate nature of this calculation, metal–metal bonding can hardly be an important factor in determining the chemical or physical properties of MGS.

In an effort to simulate more accurately the linear chains of complex ions in MGS solid, calculations were also performed on the hypothetical extended-chain structures $Pt(NH_3)_4PtCl_4Pt(NH_3)_4^{2+}$ and $[Pt(NH_3)_4PtCl_4]_2$. The results of these calculations lead to identical conclusions regarding the metal–metal interactions in MGS and, thereby, provide support for the use of the simpler ion-pair model in representing the intermolecular interactions in the solid. In particular, the Pt–Pt bond orders derived for each pair of adjacent platinum atoms in these higher polymers were essentially the same as that obtained for the ion pair. Also the distribution of energy levels followed the same pattern as in the ion pair with most of the d-like MO's occurring as essentially degenerate groups of energy levels close to the energy values of the corresponding free ion molecular orbitals. The principal exceptions were, again, the p_z- and d_{z^2}-like molecular orbitals, whose energies were distributed about the mean value of the corresponding free ion molecular orbitals. Unlike the ion-pair calculation, however, these studies indicated a very slight but probably significant deviation (0.02 eV) from the free ion values in the case of the $d_{xy,yz}$-like molecular orbitals.

In the case of a very long chain of complex ions, such as in MGS solid, these energy levels would become

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[16] W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968).

[17] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958); A. Pidcock, R. E. Richards, and L. M. Venanzi, *ibid.*, *A*, 1970 (1968).

[18] As is common practice, the MO's derived here are referred to in terms of their principal atomic orbital contributors. In the case of the so-called "d_{z^2}-like" MO's, an appreciable admixture (20–30%) of Pt 6s character was invariably found in addition to the predominant (>60%) Pt $5d_{z^2}$ atomic orbital.

[19] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 924 (1967).

[20] For $Pt(NH_3)_4PtCl_4$ this is equivalent to taking the difference in energy of the d_{z^2}-like MO's in the ion pair and the free ions, as for all other filled, metal-based MO's this energy difference is essentially zero.

bands, whose width would be determined largely by the extent of overlap between the wave functions of the individual ions. The results of our calculations suggest that this perturbation of the free ion wave functions should be most pronounced in the case of the p_z- and d_{z^2}-like orbitals. There should be substantially less effect upon the energies of the $d_{xy,yz}$-like orbitals and effectively none in the case of the d_{xy} and $d_{x^2-y^2}$-like functions. An approximate indication of the band width for the "p_z" and "d_{z^2}" bands in this solid was obtained by means of a one-dimensional tight-binding calculation in which the interactions of only the d_{z^2} and p_z atomic orbitals of the platinum atoms were considered. These calculations indicate a width of *ca.* 1.38 and 1.50 eV for the two p_z bands and *ca.* 0.62 and 0.23 eV for the d_{z^2} bands, with an energy gap of *ca.* 4.49 eV between the highest filled (d_{z^2}) and lowest empty (p_z) bands. However, it should be emphasized that the quantitative aspects of these results should not be taken too literally, in view of the severity of the approximations made in this type of calculation.[21]

As might be expected on the basis of this description of the intermolecular interactions, the degree to which the physical properties of these complexes deviate from that attributable to the individual complex ions is a sensitive function of the structural details of the solid, particularly the metal–metal separations. For example, studies of the electrical and spectral properties of a series of platinum(II) complexes related to MGS by replacement of the NH_3 hydrogens by alkyl groups have evidenced a marked dependence of the intermolecular interactions upon the metal–metal separation in the solid at distances $\leqslant \sim 3.40$ Å.[5,22] Moreover, the results of high-pressure electrical and spectral measurements on MGS and other group VIII metal complexes suggest that both inter- and intramolecular distance changes can have a substantial effect upon the properties of these materials.[1]

Our calculations on structural modifications of the $Pt(NH_3)_4PtCl_4$ unit in Figure 2 lend considerable support to this conclusion. In these calculations we have varied, independently, the distance between the two complex ions, the internuclear distances within each complex ion, and the angle between the Pt(1)–N and Pt(2)–Cl bond directions in the ion pair. The distance between the complex ions was both increased to 4.00 Å and decreased, in two increments, to 2.80 Å, which represents the approximate lower limit attained in the high-pressure experiments.

At the 4.00-Å separation we find that all the interionic orbital interactions, except for those involving the p_z atomic orbitals, are reduced to essentially negligible proportions, and even in the case of the p_z-like MO's, the deviation from the free ion energy level values amounts to only *ca.* 0.16 eV. This agrees well with the results of spectral and conductivity measurements on platinum(II) complexes structurally analogous to MGS, in that no indication of experimentally significant interionic interactions is obtained when the separation is in this range.[5,22] On the other hand, reducing this separation to 3.0 Å considerably increases the p_z and d_{z^2} orbital interactions and also produces a small but definite change in the energy of the $d_{xy,yz}$-like MO's (*ca.* 0.04 eV). The final reduction in this separation to 2.8 Å leads to a further increase in the 4a–3a, 2a–1a, and 2e–1e energy level splittings but still leaves the energies of the $d_{x^2-y^2}$- and d_{xy}-like MO's essentially unchanged relative to the free ion values. The Pt–Pt bond order calculated for the ion pair at this separation is 0.139 and arises almost entirely from σ interactions of the p_z–d_{z^2} and s–p_z atomic orbitals on the platinum atoms.

In the case of MGS solid, the bands formed by the atomic orbital overlaps should increase in width, with decreasing metal–metal separation, approximately in proportion to the change in orbital splitting observed for the ion pair. The net result will be a reduction in the gap between the lowest unoccupied "p_z" bands and the filled "$d_{xy,yz}$" and "d_{z^2}" bands. A rough measure of changes in these band gaps with metal–metal distance can be obtained by considering the changes in the 2a–3a and 1e–3a orbital separations observed in the ion-pair calculations. This is illustrated in the case of the 2a–3a (d_{z^2}–p_z) separation in curve A of Figure 5.

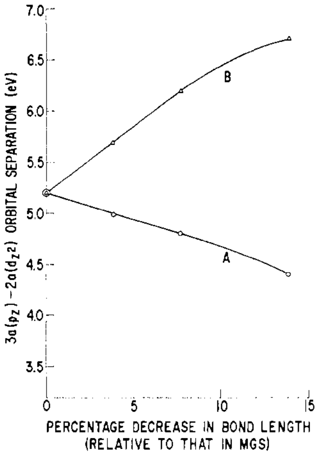

Figure 5.—The effect of a reduction in (A) the metal–metal and (B) the metal–ligand distances in $Pt(NH_3)_4PtCl_4$ upon the 2a–3a orbital separation.

Curve B of this figure illustrates the effect of changes in the internuclear distances within the complex units upon this energy level separation. In the latter calculations the distance between the complex units was maintained at 3.25 Å, while all internuclear distances within the complex ions were decreased by a fixed percentage.

The nature of the dependence upon metal–ligand distance may be understood by considering the effect of this change in distance upon the energies of the individual ion molecular orbitals. The results of such calculations show that the energies of most of the metal-like molecular orbitals, but particularly b_{1g} ($d_{x^2-y^2}$) and a_{2u} (p_z), are increased relative to those given in Table I for the unperturbed ions. These two latter orbitals are both antibonding counterparts of ligand-

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(21) In addition to the approximations made in evaluating the matrix elements in this calculation, the approach used neglects coulomb interactions between the charge carriers in the band, which can lead in some cases to unrealistic band widths: I. G. Austin and N. F. Mott, *Science*, **168**, 71 (1970). Also the "band gap" obtained from this calculation is highly dependent upon the VSIP values used for the two kinds of platinum atoms and therefore the H_{ii} charge dependence assumed in the MO calculations on the free ions.

(22) (a) P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 3763 (1965); (b) B. G. Anex, M. E. Ross, and M. W. Hedgcock, *ibid.*, **46**, 1090 (1967); (c) L. Atkinson, P. Day, and R. J. P. Williams, *Nature* (*London*), **218**, 668 (1968).

based bonding molecular orbitals and strongly reflect the increased σ- and π-type metal–ligand overlaps at the shorter metal–ligand distance. The energies of the b_{2g} (d_{xy}) and e_g ($d_{xy,yz}$) molecular orbitals are rather less affected by this change in metal–ligand distance, as these depend upon metal $d\pi$–ligand $p\pi$ type overlaps which are significantly smaller than the metal $d_{x^2-y^2}$–ligand σ and metal p_z–ligand $p\pi$ type overlaps involved in the former cases. Similarly the a_{1g} molecular orbital, which is largely metal d_{z^2} in character but also contains a significant admixture of metal s orbital, remains essentially unperturbed by this distance change due to the relatively small metal d_{z^2}–ligand σ type overlaps and the counteracting bonding effect of the metal s orbital. The net result is an increase in the a_{2u} (p_z)–a_{1g} (d_{z^2}) separation in both ions, and, therefore, a larger 2a–3a separation for the corresponding molecular orbitals in the ion pair.

The supposition that the p_z–d_{z^2} band gap in MGS solid will reflect the same kind of dependence upon internuclear distance as that deduced above for the ion pair is supported by the results of separate band structure calculations carried out using the platinum chain model described earlier. As is shown in Figure 6, this dependence is quite analogous to that found for the ion pair.

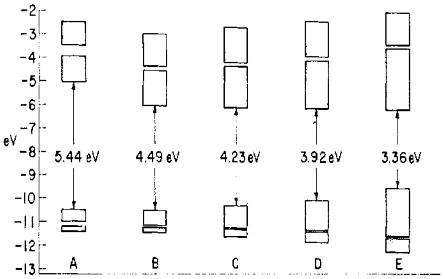

Figure 6.—The effect of internuclear distance changes upon the MGS band structure: A, the effect of decreasing the distances within the complex units (all distances but the Pt–Pt were reduced by 7.69% relative to those in MGS in deriving the H_{ii} values for Pt used in the band calculations); B, the band structure for MGS; C, Pt–Pt distance *only* reduced by 7.67%; D, Pt–Pt distance reduced by 11.0%; E, Pt–Pt distance reduced by 13.85%.

In light of these results, the fact that the electronic absorption spectrum of MGS in the visible region is strongly influenced by structural parameter changes in the solid is quite understandable. According to a recent assignment, this absorption spectrum is strongly dominated by $PtCl_4^{2-}$ ligand field transitions of the type a_{1g} (d_{z^2}), e_g ($d_{xz,yz}$), b_{2g} (d_{xy}) $\rightarrow$ b_{1g} ($d_{x^2-y^2}$).[22a] All of these, except for b_{2g} (d_{xy}) $\rightarrow$ b_{1g} ($d_{x^2-y^2}$), apparently occur at significantly lower energies as compared to their counterparts in the "free $PtCl_4^{2-}$ ion." Indeed, spectral studies of $PtCl_4^{2-}$ containing analogs of MGS with varying interionic separations and the results of spectral measurements on MGS at pressures up to *ca.* 20 kbars evidence a direct relationship between the magnitude of these spectral shifts and the interionic distance in the solid.[1] In the context of the electronic structure of MGS developed herein, the origin of this shift lies in the antibonding character of the free ion a_{1g} (d_{z^2}) – a_{1g} (d_{z^2})′ and e_g ($d_{xz,yz}$) – e_g ($d_{xz,yz}$)′ orbital interactions. These interactions give rise to crystal bands whose median energies are higher than the free ion energy levels, resulting in smaller separations between these and the relatively unperturbed b_{2g} ($d_{x^2-y^2}$) energy levels. Moreover, the magnitude of these spectral shifts clearly should depend upon the degree of intermolecular a_{1g} and e_g orbital overlap and, therefore, the metal–metal distance in the solid. On the other hand, the spectral results obtained in the case of $Pt(en)_2PtCl_4$ and K_2PtCl_4 at high pressures[1] can best be understood in terms of the intraionic distance changes occurring under pressure. In these cases, where the interionic distances are well above the 3.25 Å in MGS, and, therefore, less important in determining the electronic structure of the complex, the changes in the metal–ligand distances apparently become the dominant factor leading to an increase in energy of the d–d transitions.

The conductivity behavior of MGS under pressure[1] and the results of the experiments on alkylamine analogs of MGS[22c] can also be explained in terms of the dependence of the MGS electronic structure upon internuclear distances. It has been suggested that this conductivity could arise from carriers thermally excited from the uppermost filled d_{z^2} band to the lowest empty p_z band in these solids. On the basis of the results obtained in the MGS band structure calculations, the gap between these bands is far too great to account for the observed conductivity in this manner. On the other hand, it is quite possible that this band gap has been grossly overestimated in our calculation.[21] Also, even if these bands were widely separated, the conductivity could still arise from carriers in either the p_z or d_{z^2} bands if the origin of these carriers were extrinsic. As shall be demonstrated, a self-consistent explanation for the dependence of the MGS conductivity upon internuclear distances can be developed using the simpler intrinsic band model; however, it should be noted that these arguments will apply equally as well to a model involving relatively pressure-insensitive extrinsic donor levels close to the bottom of the p_z conduction band.

In terms of this intrinsic band model the lower conductivities of the alkylamine derivatives of MGS and the increased conductivity observed for MGS at pressures up to *ca.* 100 kbars simply reflect changes in the d_{z^2}–p_z band gap induced by the alteration in metal–metal distances. In the high-pressure experiment, however, both the metal–metal and metal–ligand distances change with increasing pressure. The net effect upon the electronic structure of the solid will depend upon such factors as the rate of change of these distances with pressure and the relative sensitivity of the electronic structure to the different types of distance changes. Furthermore, as is clear from the high-pressure spectral results obtained for $Pt(en)_2PtCl_4$ and K_2PtCl_4, the actual values of these distances are also important. For MGS, where the metal–metal distances accessible at high pressures (3.25–*ca.* 2.80 Å) are well within the region of high sensitivity and where this parameter is changing at a relatively high rate with increasing pressure as compared to the usual situation for covalent solids, it is not at all unreasonable that the metal–metal distance changes will effectively determine the conductivity behavior at low pressures. On the other hand, at higher pressures the rates of change of the metal–metal and metal–ligand distances are likely to become more comparable, and the inherently higher sensitivity of the band gap to the metal–ligand distances indicated in Figure 5 could indeed be responsible for the reversal in the conductivity *vs.* pressure curve observed for MGS above *ca.* 100 kbars.

Another structural parameter which could change as a function of pressure, yet not produce a major structural rearrangement, is the angle between the Pt–N and Pt–Cl bond directions in the adjacent complex ions. To determine what effect this might have upon the electronic structure of MGS, a calculation was also carried out on $Pt(NH_3)_4PtCl_4$ in the completely staggered configuration (*i.e.*, $\theta = 45°$ in Figure 2), in which the degree of interionic ligand–ligand interaction should be at a minimum. The interionic distance in this calculation was set at 2.80 Å. As might be expected in view of the axial symmetry of most of the platinum–platinum interactions, very little change in the energy of the d-like molecular orbitals relative to those in the $\theta = 28°$, 2.80-Å metal–metal distance case was found and the overall Pt–Pt interaction, as measured by the Mulliken bond order, was essentially the same. It is interesting that even in this optimal configuration, no δ bonding involving the d_{xy} and $d_{x^2-y^2}$ orbitals on the platinum atoms was evidenced at this interionic separation, thus effectively ruling out this type of interaction as a significant factor in determining the physical properties of MGS at any reasonable pressure.

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Magnetic Behavior of Metal Derivatives of Substituted Benzeneazo-5-pyrazolones

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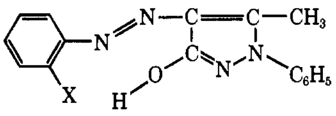
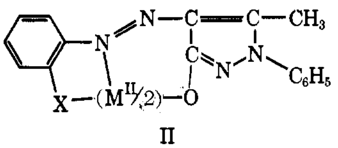
The synthesis and room-temperature magnetic moments of nickel(II), cobalt(II), and copper(II) complexes of substituted benzeneazo-5-pyrazolones and -3,5-pyrazolidinediones are reported. Cobalt(II) complexes which contain an $-SCH_3$ group in the ortho position to the azo linkage give anomalous moments, while those which contain either an $-OCH_3$ or an $-N(CH_3)_2$ group give normal, high-spin moments. Nickel(II) complexes of bidentate ligands were isolated as either high-spin or low-spin compounds depending upon the method of preparation. Anomalous moments were obtained for nickel(II) compounds which contained either a bromo or an iodo group ortho to the azo linkage. It is tentatively suggested that the coordination for nickel(II) is either tetrahedral or planar and that the ortho-bromo and ortho-iodo compounds contain both structures.

Introduction

In a rather extensive study of the coordination of divalent metal ions with azo derivatives of 3-pyrazolone[2] (I) it was shown that when $X = OCH_3$ or SCH_3 the resulting molecule is a terdentate ligand (II),



I



II

and the stability of the complex is greater than when $X = H$. However, when $X = F$, Cl, Br, I, NO_2, CH_3, or C_2H_5, the compounds behave like bidentate ligands, and the stability of the resulting metal complex is decreased for divalent nickel, cobalt, zinc, and cadmium while copper(II) compounds are not affected. Similar behavior was observed for the azo derivatives of 4-pyrazolone[3] and 5-pyrazolone.

It was suggested that the overall coordination reaction is

$$M(H_2O)_6^{2+} + 2HCh = M(Ch)_2(H_2O)_2 + 2H^+$$

and that the noncoordinating ortho substituents in the bidentate ligands interfered with the retention of water molecules. Thus, as the size of X increases, the water–metal bond length increases and the stability of the resulting complex decreases. The formation constants of divalent nickel, cobalt, zinc, and cadmium for the ortho-substituted benzeneazo-3- and -4-pyrazolones decrease in the order F, Cl, Br, I. Copper(II) complexes are insensitive to this steric effect and are therefore essentially not solvated in solution. Although the ortho-substituted azo-5-pyrazolones were too insoluble to study by potentiometric measurements, qualitative results showed the same steric effect.

Herein we report the synthesis and room-temperature magnetic moments of nickel(II), cobalt(II), and copper(II) complexes of substituted benzeneazo-5-pyrazolones (III) and -3,5-pyrazolidinediones (IV).

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(3) F. A. Snavely, N. M. Rosenblum, P. S. Danielson, and R. R. Rill, *J. Inorg. Nucl. Chem.*, **33**, 455 (1971).