Musso, *Angew. Chem. Int. Ed. Engl.*, **10**, 225 (1971); (b) H. Nakanishi, H. Morita, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **50**, 2255 (1977). For some compounds such as barbituric acid, the keto form is present in the solid state, in water as well as in CCl_4: (c) D. Voet and A. Rich, *J. Am. Chem. Soc.*, **94**, 5888 (1972); (d) P. V. Huong, F. Cruege, and J. P. Bideau, private communication. For others such as acetylacetone the proportion of the enol form increases from H_2O to MeCN and is the predominant one in nonpolar solvent. It seems that the lower concentration in enolate due to the high value of pK^H can be, at least partially, counterbalanced by the easier formation of enol. This aspect of the nitrosation reaction is now under study.

(48) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975).

Contribution from the Chemistry Department,
The Ohio State University, Columbus, Ohio 43210

Strong π-Antibonding Effects on the Electronic Structures of Complexes with Charge-Delocalized Macrocyclic Ligands

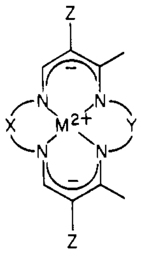
HISASHI OKAWA and DARYLE H. BUSCH*[1]

Received September 7, 1978

The complexes of copper(II) with the 14-, 15-, and 16-membered, charge-delocalized, dianionic macrocycles $Me_2[14-16]tetraenatoN_4^{2-}$ exhibit a number of properties that are attributable to the presence of strong ligand–metal π interactions of an antibonding nature. These include d–d transitions in their electronic spectra, which occur at remarkably low energies, and the ESR spectral parameters for these compounds. The square-planar complexes show no tendency to add axial ligands in strongly coordinating solvents. The strong π-antibonding, as differentiated from π-bonding, interactions generate the distinctive qualities of these complexes. For example, the presence of low-energy vacant π orbitals in metal porphyrins contributes to their rich patterns of reduction. In contrast, the complexes of the class discussed here are difficult to reduce.

Introduction

The investigation of the effect of substituents on the electronic spectral and electrochemical properties of complexes having structure I has shown that the changes in electron density that occur on the ligand are transmitted directly to the metal ion.[2] Thus the use of substituents affords a powerful technique for controlling the electronic character of the donor atoms without altering the stereochemistry of the coordination sphere. The possibilities opened by such control are well illustrated by the recent report that the presence of acetyl substituents on the γ-carbon atoms of bis(acetylacetone) ethylenediimine produces a cobalt(II) complex whose O_2 adduct is stable at room temperature.[3] This contrasts with the usual behavior of such Schiff base complexes since their O_2 adducts are generally formed only at low temperatures.[4] The unsubstituted macrocycles of structure I with Z = H may be viewed as the parents of all compounds having structure I.



I

This key role of these unsubstituted species causes us to be especially interested in their electronic structures. We report here the syntheses of the copper(II) complexes, $Cu^{II}(Me_2[14-16]tetraenatoN_4)$, and the results of physical studies with emphasis on their electronic and ESR spectra. The complexes are unusual in that their electronic spectra exhibit d–d transitions at unusually low energies. The assignment of these bands leads to the conclusion that a very strong π interaction exists between the e_g orbitals of the metal ion and the filled ligand π orbitals. The assignments are entirely consistent with the results of ESR studies. Thus, the unsubstituted ligands of this class (structure I) are very strong π donors, as well as strong σ donors. This description of electronic structure also accounts for the relatively slight tendency of the four-coordinate planar complexes of these ligands to expand their coordination numbers. Previous studies have remarked on the difficulty of producing five- and six-coordinate structures by the addition of axial ligands.[5,6]

Table I. Visible Spectral Data (cm^{-1} (ε)) for $H_2(Me_2[n]tetraenatoN_4)$ and $Cu(Me_2[n]tetraenatoN_4)$[a]

$H_2(Me_2[14]tetraenatoN_4)$	29 500 (sh, ~4000), 32 300 (30 100), 33 670 (27 200)
$H_2(Me_2[15]tetraenatoN_4)$	30 300 (sh, ~6400), 33 560 (26 600)
$Cu(Me_2[14]tetraenatoN_4)$	16 100 (165), 20 000 (sh, 200), 29 400 (32 200), 32 600 (26 900)
$Cu(Me_2[15]tetraenatoN_4)$	13 300 (136), 18 100 (155), 27 000 (sh, 7100), 29 600 (26 900), 31 000 (9900)
$Cu(Me_2[16]tetraenatoN_4)$	11 800 (215), 18 000 (200), 24 000 (2300), 28 800 (23 700), 31 000 (sh, 8400)

[a] n = 14, 15, and 16.

Results and Discussion

The procedures used in the synthesis of $Cu(Me_2[14-16]tetraenatoN_4)$ are unremarkable; however, the products require protection from the air. Elemental analyses, parent ion peaks in the mass spectra, and infrared spectra confirm the assigned structures.

The electronic spectra (chloroform solution) of the complexes show three features assignable as arising from d–d transitions (Table I). This includes two absorption bands in the region 10–20 $cm^{-1} \times 10^3$ and a third band that is partially obscured by strong intraligand and/or charge-transfer bands. By comparison of the spectra of the complexes with those of the neutral free ligands, $H_2(Me_2[14,15]tetraenatoN_4)$, a band at about 24 $cm^{-1} \times 10^3$ is assigned as a d–d transition for $Cu(Me_2[16]tetraenatoN_4)$ and one at about 27 $cm^{-1} \times 10^3$ for $Cu(Me_2[15]tetraenatoN_4)$. The corresponding absorption is not resolved in the case of the 14-membered ring derivative. The spectra of $H_2(Me_2[15]tetraenatoN_4)$ and $Cu(Me_2[15]tetraenatoN_4)$ are shown in Figure 1. Most notably, the d–d bands shift toward higher energy as the size of the macrocyclic ring decreases. On the basis of the shifts observed, the third band for $Cu(Me_2[14]tetraenatoN_4)$ would be expected to occur at 29–33 $cm^{-1} \times 10^3$. This would place it in the same region

0020-1669/79/1318-1555$01.00/0

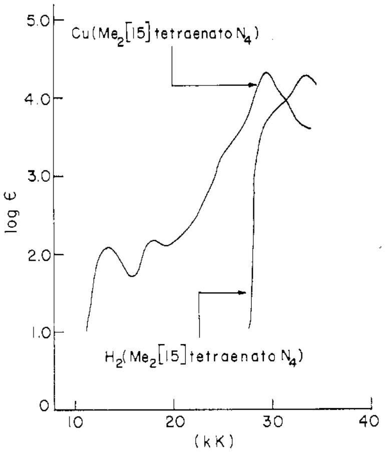


Figure 1. Electronic spectra of the macrocyclic ligand H_2[Me-[15]tetraenatoN_4) and its copper(II) complex.

as strong ligand absorptions (Table I). It is also significant that the d–d bands occur at lower energies than those normally observed for Cu^{2+}. For example, the low-energy band for $Cu(en)_2X_2$ ($X^- = BF_4^-, ClO_4^-, SCN^-$) is found[7] near 18.5 $cm^{-1} \times 10^3$ and that for $Cu(bpy)_2(ClO_4)_2$ is estimated at about 20 $cm^{-1} \times 10^3$.[8] It is, of course, well-known[9–12] that the low-energy transition assigned to $b_{1g} \leftarrow a_{1g}$ shifts to lower energy when fifth and sixth ligands are added; e.g., this band is found at 14.3 $cm^{-1} \times 10^3$ for $Cu(NH_3)_4(NCS)_2$. The spectra of the subject complexes have been measured in both nonpolar ($CHCl_3$) and polar solvents (EtOH, DMF, Me_2SO, py), and the band positions are independent of solvent. Further, the spectra obtained on solid samples agree completely with those measured on solutions. These results clearly substantiate the four-coordinate, planar configuration of these complexes in the solid state and in solution, even in polar solvents. Accordingly, the low energies of the first d–d bands cannot be ascribed to higher coordination numbers.

The usual sequence of d orbitals assumed in discussions of strong field planar copper(II) complexes is $b_{1g}(d_{x^2-y^2}) > b_{2g}(d_{xy}) > a_{1g}(d_{z^2}) > e_g(d_{xz}d_{yz})$. In fact, the orbital order $b_{1g} > b_{2g} > e_g$ (with the position of a_{1g} depending on the axial ligands) has been demonstrated by polarized spectra studies for tetragonal complexes.[13] Such sequences of energy levels appear to be generally valid for complexes in which little or no π bonding occurs.

For the present cases, the assignment of the lowest energy band to the transition from b_{1g} to b_{2g} is untenable because energy values of 11.8 $cm^{-1} \times 10^3$ (for Cu(Me$_2$[16]-tetraenatoN$_4$)) and 13.3 $cm^{-1} \times 10^3$ (for Cu(Me$_2$[15]-tetraenatoN$_4$)) are too low. This transition corresponds to $10Dq^{xy}$ and it is irrational to assign such low values to this parameter for these square planar complexes (compare to 18.5 $cm^{-1} \times 10^3$ for $Cu(en)_2X_2$).[7] The most consistent interpretation follows from the assumption of the orbital order $b_{1g} > e_g > b_{2g}$ (a_{1g} may fall between e_g and b_{2g}). Such a sequence of energy levels is expected to occur when the ligands exert both strong σ-bonding effects and strong π-antibonding effects.

The e_g orbitals of the Cu^{2+} ion will interact with either or both the filled π and vacant π* orbitals of the ligand, depending on their relative energies. The behavior observed here requires strong interaction with the filled ligand π orbitals. This produces e_g orbitals that are antibonding in character but are still predominantly metal d orbitals. The result is displacement of the e_g orbitals toward higher energy relative to b_{2g} and a_{1g}. A qualitative molecular orbital diagram is shown in Figure 2. From this model, the three d–d bands are assigned to the transitions $b_{1g}(\sigma^*) \leftarrow e_g(\pi^*)$, $b_{1g}(\sigma^*) \leftarrow a_{1g}(\sigma^*)$, and $b_{1g}(\sigma^*) \leftarrow b_{2g}$. Note that the metal ion b_{2g} orbital is essentially nonbonding since the ligand has no in-plane π orbitals with which it may interact.[14,15] The decreasing energy of the transition $b_{1g}(\sigma^*) \leftarrow e_g(\pi^*)$ as the size of the macrocyclic ring increases is consistent with the behavior observed for simpler macrocyclic ligands.[16,17] For the present case, the effect of ring size on energy is dominated by changes in the σ bonding. Dominance by the change in π bonding would have the opposite effect. It is therefore concluded that a strong π-antibonding interaction is present for all these complexes.

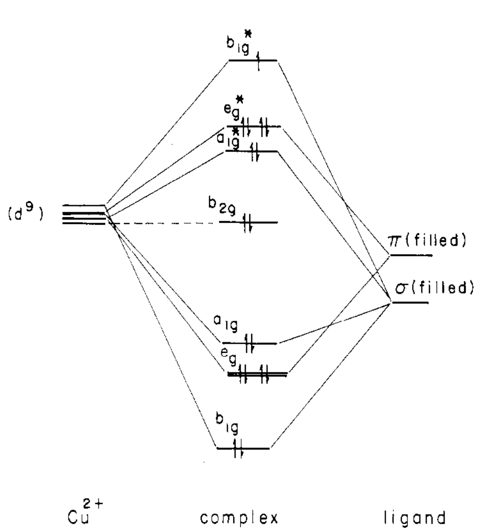


Figure 2. Simplified molecular orbital diagram for the copper(II) complexes.

Table II. ESR Parameters and Magnetic Moments of Copper(II) Complexes[a]

	$g_\parallel$	$g_\perp$	A, cm^{-1} [b]	μ_{eff} (K)	ref
Cu(Me$_2$[14]tetraenatoN$_4$)	2.127	2.036	−0.0217	1.77 (299.7)	*c*
Cu(Me$_2$[15]tetraenatoN$_4$)	2.153	2.047	−0.0207	1.80 (299.6)	*c*
Cu(Me$_2$[16]tetraenatoN$_4$)	2.156	2.051	−0.0193	1.81 (299.6)	*c*
Cu(acac)$_2$	2.2661	2.0535	−0.0160		17
Cu(sal-im)$_2$	2.2004	2.0450	−0.0185		17
Cu(salen)	2.186	2.042			25
Cu(sal-oxime)$_2$	2.22	2.12	−0.0163		24
Cu(sal-amide)$_2$	2.22	2.12	−0.0156		25
Cu(biuret)$_2$	2.22	2.09	−0.0158		25
Cu(phthalocyanine)	2.1746	2.0450	−0.0202		18

[a] Ligand abbreviations refer to structure I; the number in brackets indicates ring size. [b] Copper hyperfine coupling constant. [c] This work.

The ESR spectra of these complexes in frozen dichloromethane solutions show axial symmetry. This implies that their structures may be approximated by D_{4h} or C_{4v} symmetries, although their true symmetries are no higher than D_{2h} or even C_2. The hyperfine splittings due to the nuclear spin of copper are observed but the superhyperfine splittings expected to arise from coupling to the nuclear spins of the nitrogen atoms were not observed. Values for the ESR parameters are given in Table II, along with magnetic moments determined at room temperature. In order to facilitate comparison, ESR parameters are also included for a few other compounds of copper. The values of $g_\perp$ were calculated in the usual way from g_{av} and $g_\parallel$, where g_{av} was obtained from the solution spectra at room temperature. The magnetic moments agree within experimental error with the values calculated from the equation $\mu_{eff} = g(S(S+1))^{1/2}$, with the use of the experimental g_{av} values. Calculated values for μ_{eff}: Cu(Me$_2$[14]tetraenatoN$_4$), 1.787β; Cu(Me$_2$[15]tetraenatoN$_4$), 1.801β; Cu(Me$_2$[16]tetraenatoN$_4$), 1.804β. This again supports the conclusion that the molecular structures of the complexes are the same in the solid state and in solution. The parameters for the complexes of immediate interest here approximate those for the long known macrocyclic complex (phthalocyanine)copper(II).[18] However, the new complexes do provide extreme data; e.g., Cu(Me$_2$[14]tetraenatoN$_4$) has notably small values for $g_{\|}$ and $g_{\perp}$.

A simplified molecular orbital model[17,18] formulates the anisotropic **g** tensors as in eq 1 and 2, where g_0 has the free

$$g_{\|} = g_0 - 8\lambda_0\alpha^2\beta_1{}^2/\Delta(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy}) \tag{1}$$

$$g_{\perp} = g_0 - 2\lambda_0\alpha^2\beta^2/(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xz}, \mathrm{d}_{yz}) \tag{2}$$

electron value, λ_0 is the spin–orbit coupling constant for the free copper(II) ion (828 cm^{-1}), and $\Delta(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy})$ and $\Delta(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy}, \mathrm{d}_{yz})$ are energy separations. The coefficients α, β, and β_1 are defined for the wave functions

$$^2\mathrm{B}_{1g}\text{:}\ \ \alpha\mathrm{d}_{x^2-y^2} - (\alpha'/2)(-\sigma_x{}^{\mathrm{a}} + \sigma_y{}^{\mathrm{b}} + \sigma_x{}^{\mathrm{c}} - \sigma_y{}^{\mathrm{d}})$$

$$^2\mathrm{E}_{g}\text{:}\ \ \beta\mathrm{d}_{xz} - [(1 - \beta^2)/2](\mathrm{p}_z{}^{\mathrm{a}} - \mathrm{p}_z{}^{\mathrm{c}})$$

$$^2\mathrm{B}_{2g}\text{:}\ \ \beta_1\mathrm{d}_{xy} - [(1 - \beta_1{}^2)/2](\mathrm{p}_y{}^{\mathrm{a}} + \mathrm{p}_x{}^{\mathrm{b}} - \mathrm{p}_y{}^{\mathrm{c}} - \mathrm{p}_x{}^{\mathrm{d}})$$

From these formulations and experimental parameters, the coefficients α^2 and β^2 may be evaluated. $\beta_1{}^2$ is taken as unity since there are no appropriate ligand orbitals to combine with d_{xy} of Cu^{2+}. First, from $g_{\|}$ and the (approximate) spectroscopic value of $\Delta(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy})$, α^2 is calculated to have the following values: Cu(Me$_2$[14]tetraenatoN$_4$), 0.57; Cu(Me$_2$[15]tetraenatoN$_4$), 0.62; Cu(Me$_2$[16]tetraenatoN$_4$), 0.56. The experimental values of $\Delta(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xz,yz})$ are more precisely known so that they and $g_{\perp}$ give good estimates of $\alpha^2\beta^2$. Then from the values for $\alpha^2\beta^2$ and α^2, β^2 is readily estimated. Calculated values for $\alpha^2\beta^2$, β^2: Cu(Me$_2$[14]tetraenatoN$_4$) 0.324, 0.57; Cu(Me$_2$[15]tetraenatoN$_4$) 0.361, 0.59; Cu(Me$_2$[16]tetraenatoN$_4$) 0.344, 0.62. These values all indicate substantial covalent interaction both in the σ- and π-electron systems.

Reciprocally, the magnitudes of $g_{\|}$ and $g_{\perp}$ can be explained satisfactorily in terms of the same molecular orbital diagram that was used to discuss the electronic spectra. Recall that the values of $g_{\perp}$ and $g_{\|}$ are at the lower extreme of those observed for planar copper(II) complexes. The value of $g_{\|}$ is small because (a) the strong σ covalency causes α^2 to be small and (b) the greatly destabilized σ^* orbital ($\mathrm{d}_{x^2-y^2}$) makes $\Delta(\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy})$ large, since d_{xy} is nonbonding. The value of $g_{\perp}$ is small because $\alpha^2\beta^2$ is very small, which results, in turn, from both strong σ and π interactions. Indeed it has been demonstrated that small $g_{\|}$ and small $g_{\perp}$ are associated with strong covalent bonding.[2] The variation of both $g_{\|}$ and $g_{\perp}$ with ring size among these complexes results mostly from changes in the energy intervals. The covalent character does not change greatly; i.e., α^2 has values of 0.57, 0.62, and 0.56.

The electronic structures of the unsubstituted tetraenato complexes discussed here appear to differ most strongly from those of the corresponding porphyrin and phthalocyanine complexes in the relative importance of the interactions with the filled π-bonding and vacant π-antibonding orbitals of the ligands. The significance of the vacant π-antibonding orbitals of the latter is well established. For example, electrons are readily accommodated in the π-antibonding orbitals of (phthalocyanine)copper(II) or (aetioporphyrin IV)copper(II), and stepwise reduction produces mono-, di-, and trinegative species.[19-21] In contrast, metal complexes of Me$_2$[14–16]tetraenatoN$_4$ are relatively difficult to reduce.[22] These facts along with the visible and ESR spectral properties suggest that the interaction of the Cu^{2+} e$_g$ orbitals with the filled π ligand orbitals is far more important than their interaction with vacant π-antibonding ligand orbitals for Cu(Me$_2$[14–16]tetraenatoN$_4$). This viewpoint implies that the π-antibonding orbitals of the ligand lie at high energies. In support of that suggestion, the neutral ligands show no electronic transitions at energies lower than 30 cm^{-1} × 10^3, with their major peaks at 30–35 cm^{-1} × 10^3, whereas the intense (Soret) bands of the porphyrins and phthalocyanines fall in the neighborhood of 25 cm^{-1} × 10^3. The general failure of the copper atom in these complexes to add fifth and sixth ligands may also be rationalized in terms of the relatively great buildup of electron density on the metal atom that results from the ligand donating electron density through both its σ- and π-electron systems.

Experimental Section

Physical Measurements. Visible spectra were recorded on a Cary Model 14R recording spectrophotometer with chloroform, ethanol, *N,N*-dimethylformamide, dimethyl sulfoxide, and pyridine solutions or mulls dispersed on filter paper impregnated with Halocarbon 25-S5 grease (Halocarbon Product Corp.). Infrared spectra were measured on a Perkin-Elmer Model 337 recording spectrophotometer with Nujol mulls pressed between KBr disks. Magnetic susceptibilities in the solid state were determined at room temperature by the Faraday method.[23] Magnetic moments were determined by the expression $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{A}}T)^{1/2}$, where χ_{A} is the molar susceptibility corrected by the use of Pascal's constants. The ESR spectra (X band) were measured in dichloromethane at room temperature and at liquid nitrogen temperature (frozen solution) with a Varian V4500-10A spectrometer equipped with a dual cavity. A sample of DPPH was placed in the reference cavity. Mass spectra were obtained with a MS-9 spectrometer at an ionizing potential of 70 eV. Elemental analyses were performed by Galbraith Laboratories, Inc.

Syntheses. Synthetic procedures for obtaining the ligand hexafluorophosphates [H$_4$(Me$_2$[14–16]tetraenatoN$_4$)](PF$_6$)$_2$ and the neutral ligands H$_2$(Me$_2$[14–16]tetraenatoN$_4$) are reported elsewhere.[5,6] All complexes were prepared under nitrogen in a glovebox.

Cu(Me$_2$[14]tetraenatoN$_4$). Copper acetate monohydrate (2.0 g) and [H$_4$(Me$_2$[14]tetraenatoN$_4$)](PF$_6$)$_2$ (5.12 g) were suspended in absolute ethanol (100 mL). To this was added potassium *tert*-butoxide (4.5 g), and the ethanolic mixture was heated gently with stirring for 1 h. After the inorganic particles were eliminated by filtration, the solvent was removed by evaporation. The residue was extracted with benzene (100 mL), and the benzene solution was filtered and concentrated to about 20 mL to give the product as green prisms. The solid was collected by filtration and recrystallized from benzene. Anal. Calcd for C$_{12}$H$_{18}$N$_4$Cu: C, 51.14; H, 6.44; N, 19.88; Cu, 22.54. Found: C, 51.37; H, 6.56; N, 20.01; Cu, 22.30. Mol wt 281.8. MS: *m/e* 281, 282, 283, 284, 285.

Cu(Me$_2$[15]tetraenatoN$_4$). This complex was obtained by refluxing an ethanolic solution (100 mL) containing [H$_4$(Me$_2$[15]tetraenatoN$_4$)](PF$_6$)$_2$ (5.3 g), copper(II) acetate monohydrate (2.0 g), and potassium *tert*-butoxide (4.5 g) for 40 min. The crude product was recrystallized from benzene as deep purple prisms. Anal. Calcd for C$_{13}$H$_{20}$N$_4$Cu: C, 52.77; H, 6.81; N, 18.99; Cu, 21.48. Found: C, 53.05; H, 7.00; N, 19.11; Cu, 21.16. Mol wt 295.9. MS: *m/e* 295, 296, 297, 298, 299.

Cu(Me$_2$[16]tetraenatoN$_4$). A solution containing [H$_4$(Me$_2$[16]tetraenatoN$_4$)](PF$_6$)$_2$ (5.4 g), copper acetate monohydrate (2.0 g), and potassium *tert*-butoxide (4.5 g) in absolute ethanol (100 mL) was refluxed gently for 15 min. After filtration, the solution was concentrated to dryness, and the residue was extracted with ether (100 mL). The ether extract was passed through an aluminum oxide column and then concentrated to give red-purple prisms. Anal. Calcd for C$_{14}$H$_{22}$N$_4$Cu: C, 54.26; H, 7.16; N, 18.08; Cu, 20.50. Found: C, 54.01; H, 7.18; N, 17.88; Cu, 20.19. Mol wt 309.9. MS: *m/e* 309, 310, 311, 312, 313.

Acknowledgment. This research was supported in part by a grant from the Ministry of Education of Japan and in part by the U.S. National Science Foundation.

Registry No. Cu(Me$_2$[14]tetraenatoN$_4$), 69897-20-7; Cu(Me$_2$[15]tetraenatoN$_4$), 69897-21-8; Cu(Me$_2$[16]tetraenatoN$_4$), 69942-18-3; H$_2$(Me$_2$[14]tetraenatoN$_4$), 59129-94-1; H$_2$(Me$_2$[15]tetraenatoN$_4$), 59129-95-2.

References and Notes

(1) To whom correspondence should be addressed.

(2) D. G. Pillsbury and D. H. Busch, *J. Am. Chem. Soc.*, **98**, 7836 (1976).
(3) K. Kubokura, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **51** (7), 2036 (1978).
(4) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).
(5) D. P. Riley, J. A. Stone, and D. H. Busch, *J. Am. Chem. Soc.*, **98**, 1752 (1976).
(6) D. P. Riley, Ph.D. Thesis, The Ohio State University, 1975.
(7) B. J. Hathaway, D. E. Billing, P. Nicholls, and I. M. Proctor, *J. Chem. Soc. A*, 319 (1969).
(8) B. J. Hathaway, I. M. Proctor, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 2219 (1969).
(9) M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, **40**, 27 (1957).
(10) B. R. James, M. Parris, and R. J. P. Williams, *J. Chem. Soc.*, 4630 (1961).
(11) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).
(12) A. A. G. Tomlinson, B. J. Hathaway, D. E. Billing, and P. Nicholls, *J. Chem. Soc. A*, 65 (1969).
(13) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
(14) R. J. Dudley, R. J. Fereday, B. J. Hathaway, and P. G. Hodgson, *J. Chem. Soc., Dalton Trans.*, 1341 (1972).
(15) C. M. Cuzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. A*, 2299 (1969).
(16) L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4029 (1977).
(17) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).
(18) D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).
(19) J. W. Dodd and N. S. Hush, *J. Chem. Soc.*, 4607 (1964).
(20) D. W. Clark and N. S. Hush, *J. Am. Chem. Soc.*, **87**, 4238 (1965).
(21) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966).
(22) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).
(23) V. Katovic, L. Lindoy, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).
(24) A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 983 (1964).
(25) G. M. Larin, G. V. Panova, and E. G. Rukhadze, *J. Struct. Chem.* (*Engl. Transl.*), **6**, 664 (1965).

Contribution from the Department of Chemistry,
University of Calgary, Calgary, Alberta, Canada, T2N 1N4

A Theoretical Study of the Ethylene–Metal Bond in Complexes between Cu^+, Ag^+, Au^+, Pt^0, or Pt^{2+} and Ethylene, Based on the Hartree–Fock–Slater Transition-State Method

TOM ZIEGLER and ARVI RAUK*

Received December 4, 1978

An analysis based on the Hartree–Fock–Slater transition-state method is given of the metal–ethylene bond in the ion–ethylene complexes $Cu^+–C_2H_4$, $Ag^+–C_2H_4$, and $Au^+–C_2H_4$ as well as in complexes with $PtCl_3^-$ and $Pt(PH_3)_2$. The contribution from σ donation to the bonding energy was found to be equally important for all three complexes with the ions, whereas the contribution from the π back-donation was found to be important only for the Cu complex. A similar analysis of $Pt(Cl)_3^-–C_2H_4$ and $Pt(PH_3)_2–C_2H_4$ showed that the position of ethylene perpendicular to the coordination plane of $Pt(Cl)_3^-$ in Zeise's salt is caused by steric factors, whereas the position of ethylene in $Pt(PH_3)_2–C_2H_4$ is due to electronic factors, specificially π back-donations.

1. Introduction

The bonding in transition-metal complexes has come under close scrutiny in recent years by the powerful combination of semiempirical calculations and use of simple perturbation theory (PMO) as employed by Hoffmann and his co-workers, as well as others.[1] Such systems, because of their size, are not readily amenable to study by ab initio methods, although a number of attempts have been made when advantage could be taken of high symmetry. Hartree–Fock calculations are very time consuming and artifacts introduced as a consequence of unavoidable limitations of the basis set and neglect of electron correlation are not readily identified and ruled out. Although the faster Hartree–Fock–Slater (HFS) method, using the transition-state approximation,[2] has been used numerous times[3-5] with considerable success for the calculation of ionization potentials and electronic excitation energies, little insight has yet been achieved for bonding schemes, interaction energies, or charge distributions. Particularly in the area of organometallic complexes, where one is interested in catalytic activity, accurate knowledge of bond strengths, modes of bonding, charge distributions, force constants, and oxidation states is desirable. It is especially desirable to obtain the same data for a series of complexes or metals so that systematic errors which inevitably occur in any computational model will tend to cancel.

We have recently proposed a scheme within the HFS framework based on a transition-state method for the computation of bond energies.[6] The scheme naturally yields an analysis of the contributions to bond strengths in terms such as steric and electrostatic interaction and σ- and π-electron donation, which are in common parlance for simpler organic and inorganic systems. It also provides ready identification in PMO language of the fragment molecular orbitals which interact to form bonds and determine conformational preferences. Initial calculations on some diatomic molecules and a few transition-metal complexes gave results in better agreement with experiment than have yet been achieved by the Hartree–Fock method[6] (and with considerably less computational effort).

We present below a brief outline of the scheme presented in detail elsewhere[6] and then present a detailed analysis of the coordination between ethylene and the transition-metal ions or fragments Cu^+, Ag^+, Au^+, $PtCl_3^-$, and $Pt(PH_3)_2$.

2. Theory

2.1. Transition-State Method for the Calculation of Bonding Energies by the Hartree–Fock–Slater Method. Consider the molecule $\overline{AB}$, with electronic density $\rho_{(AB)}$, where the subscript (AB) indicates that the molecule is formed from the two electronic systems (molecules) A and B with densities ρ_A and ρ_B, respectively. If the molecules A and B are described by the occupied and virtual orbitals $\{U_i^\alpha, U_i^\beta\}$ where α and β indicate electrons of spin up and spin down, then one might write

$$\rho_{AB} = \rho_A + \rho_B = \sum_i^{occ} P_{ii}^\alpha \cdot U_i^\alpha(\vec{r}_1) \cdot U_i^\alpha(\vec{r}_1) + \sum_i^{occ} P_{ii}^\beta \cdot U_i^\beta(\vec{r}_1) \cdot U_i^\beta(\vec{r}_1) \quad (2.1)$$

and

$$\rho_{(AB)} = \sum_{ij} (P_{ij}^\alpha \cdot \delta_{ij} + \Delta P_{ij}^\alpha) U_i^\alpha(\vec{r}_1) \cdot U_j^\alpha(\vec{r}_1) + \sum_{ij} (P_{ij}^\beta \cdot \delta_{ij} + \Delta P_{ij}^\beta) U_i^\beta(\vec{r}_1) \cdot U_j^\beta(\vec{r}_1) \quad (2.2)$$

where P_{ii} is the bond order matrix for $\rho_A + \rho_B$ (A and B at infinite separation) and $P_{ij} \cdot \delta_{ij} + \Delta P_{ij}$ the bond order matrix for $\rho_{(AB)}$, both with respect to the basis $\{U_i\}$.

0020-1669/79/1318-1558$01.00/0