Acta Cryst. (1976). A32, 353

Theoretical Calculations of Deformation Densities in Some Transition Metal Complexes

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(*Received* 24 *October* 1975; *accepted* 7 *November* 1975)

Theoretical deformation densities for $Ni(CH_3)_2$, MnO_4^- and CoO_6^{10-} have been calculated by *ab initio* Hartree–Fock and configuration interaction methods. Peaks similar to those found in diffraction experiments at short distances from the transition metal atoms are observed. They can be interpreted in terms of the specific electronic occupations of the *d* orbitals.

Introduction

A growing interest in deviations from atomic sphericity in crystals has occurred with the increasingly accurate measurement of electron density distributions from diffraction data. From the deformation, or residual, density (defined here as the difference between the electron density distribution in a molecular system and the corresponding density obtained from a superposition of the constituent spherically averaged atoms) σ-bonds, π-bonds, bent-bonds, lone-pair electrons and the like may be recognized. Some recent investigations (Rees & Coppens, 1973; Iwata & Saito, 1973; Marumo, Isobe, Saito, Yagi & Akimoto, 1974) have also demonstrated deformation density features in the vicinity of transition metal atoms. These departures from sphericity are probably very common and should be observable from the results of many crystal structure determinations. Some have undoubtedly already been observed but discarded as being spurious peaks arising from systematic data measurement errors. The present investigation treats theoretically three rather different transition metal complexes: $Ni(CH_3)_2$, MnO_4^- and CoO_6^{10-}. The first is neutral and covalent, the second is a covalent ion and the third is a highly ionic cluster. All three exhibit pronounced deformation densities close to the metal atoms.

Calculations

Details of the calculations have been, or will be, published elsewhere (Johansen, 1972; Johansen & Roos, 1974; Wahlgren & Johansen, 1976; Johansen, Roos, Wahlgren & Åkermark, 1976). Only a short account of them is given here. They were all *ab initio* calculations of Hartree–Fock type, but in two cases they included a limited configuration interaction treatment. The basis sets used were composed of contracted Gaussian-type orbitals. These were of only fair quality for $Ni(CH_3)_2$ but of very good quality for both MnO_4^- and CoO_6^{10-} (Table 1). The results from closed-shell calculations are presented for $Ni(CH_3)_2$ and MnO_4^- and those from open-shell investigations for $Ni(CH_3)_2$ and CoO_6^{10-}. The configuration interaction calculations included all configurations originating from redistributions in a limited set of the filled and empty valence orbitals. Details are given in the references quoted above. CoO_6^{10-} was treated as an ionic crystal comprising Co^{2+} and O^{2-} ions, the cluster being surrounded by 50 point charges chosen by a least-squares fit to give the ionic Madelung potential at the cluster site.

Table 1. *Basis sets*

	Primitive functions				Contracted functions			
	s	*p*	*d*	Total	*s*	*p*	*d*	Total
$Ni(CH_3)_2$				115				60
Ni	11	8	4		6	4	2	
C	7	3			4	2		
H	4				2			
MnO_4^-				203				105
Mn	16	13	6		10	7	3	
O	10	6			5	3		
CoO_6^{10-}				215				116
Co	14	9	5		8	4	3	
O	9	5			4	3		

The difference electron density distributions were calculated making use of the symmetries of the complexes and of one or two interpolations, so that the contours are based upon a final 160 by 160 grid. To depict satisfactorily both small and large density differences on the same maps, the density at each contour is double that of its neighbour, so that the difference in levels is not constant. This contrasts with the representations from most experimental results and should be taken into account in making comparisons. The conventional unit of length in quantum chemical calculations is a Bohr radius [1 atomic unit (a.u.)= 0·529166 Å]. Thus the electron density contours are in units of electrons per cubic atomic unit, where 1 e $(a.u.)^{-3} = 6{\cdot}74876$ e Å^{-3}.

In each case the deformation density was formed by taking the difference between the electron density calculated for the molecule or ion and that for a superposition of the constituent atoms, where the density for each atom was determined from exactly the same contracted basis set as that employed in the molecular calculation. The atoms were taken to be neutral and in their ground states, and the densities for the partly occupied shells were spherically averaged. Thus the deformation densities for MnO_4^- and CoO_6^{10-}, when integrated over all space, represent the distributions of net total charges of 1 e and 10 e respectively.

It should be noted that other references could equally well have been used instead of the neutral atoms. Several investigations, for example with Co^{2+} and O^{2-} as references, were in fact performed to test the effect of the choice of atomic densities. These all showed that, although the qualitative features of the deformation density in the vicinity of the metal atom do not change substantially, and therefore that the conclusions drawn from the present work are not affected, the distribution in other regions depends rather sensitively upon the reference. Ambiguities with respect to the reference system clearly require detailed study, both from the theoretical and experimental sides.

In the density maps of the present investigation, fully drawn contours show where electron density has increased, and broken lines where it has decreased after formation of the molecule or ion.

Results and discussion

Fig. 1 shows the deformation density for $Ni(CH_3)_2$ in the closed-shell low-spin $^1A_1$ state with the Hartree–Fock approximation, while Fig. 2 shows the corresponding density for the same molecule in the high-spin $^3B_1$ ground state for which a limited configuration interaction scheme has been employed. The eclipsed conformation of $Ni(CH_3)_2$ was chosen (Johansen *et al.*, 1976). The configuration interaction turned out not to alter the deformation density for the $^3B_1$ state significantly, and this refinement can, therefore, be left out of the discussion here. For both states there is excess density (peak heights 0·5–1·0 e Å^{-3}) in regions located at distances of 0·42 Å from the Ni atom and deficiency in the Ni–C bond directions. This is a distribution quite similar to that found experimentally for γ-Ni_2SiO_4 (Marumo *et al.*, 1974). The peaks occur at different positions for the two electronic states, and this, therefore, opens interesting new possibilities. It remains, however, to be seen whether information of this type, obtained from diffraction measurements, can be used to determine experimentally the electronic state of a transition metal atom in a particular crystal.

The peaks for the $^1A_1$ state arise from the filling of the xy, xz and yz orbitals (the coordinate systems used are shown in the density maps) at the expense of the x^2-y^2 orbital. Similarly, the peaks in the $^3B_1$ state are due to filled xy and yz orbitals, an almost filled z^2 orbital and a deficiency in the x^2-y^2 and xz orbitals. It should also be noted that there seems to be a significant difference between the deformation density for the 'aliphatic' C–H bond in $Ni(CH_3)_2$ and the more 'aromatic' bond in TCNQ (Johansen, 1975).

The deformation density for the permanganate ion in the $^1A_1$ closed-shell ground state is shown in Fig. 3. Apart from illustrating a build-up of charge along the bond and the formation of lone-pairs on the O atoms, the figure again shows pronounced peaks close to the transition metal atom. They are at distances of 0·30 Å from the Mn nuclear position and have peak height maxima of about 2 e Å^{-3}. In this case they arise from excess charge in the xy, xz and yz orbitals and deficiency in the x^2-y^2 and z^2 orbitals.

Finally Fig. 4 shows the deformation density for CoO_6^{10-} in the $^4T_{1g}$ ground state, the calculation having included a limited configuration interaction. Again

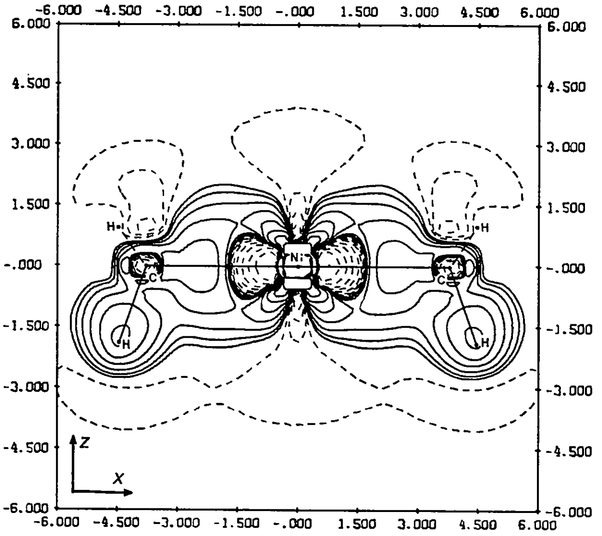

Fig. 1. Deformation density for $Ni(CH_3)_2$ in the low-spin $^1A_1$ state obtained from a Hartree–Fock type calculation. xz-plane; first contours respectively ±0·0025 e (a.u.)$^{-3}$; neighbouring contours differ by a factor of 2.

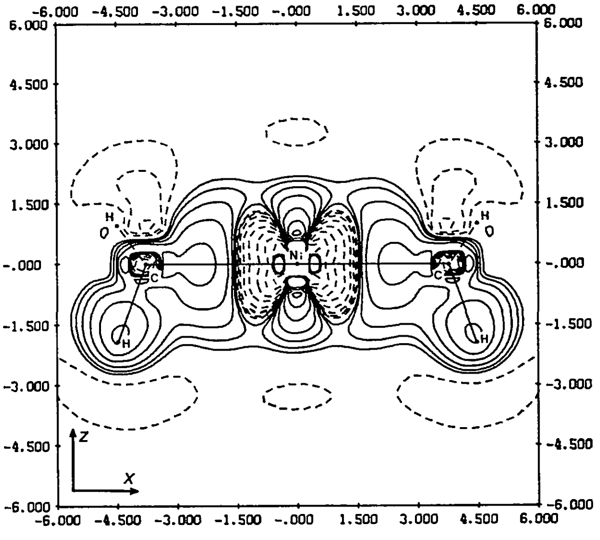

Fig. 2. Deformation density for $Ni(CH_3)_2$ in the high-spin $^3B_1$ state obtained from a limited configuration interaction calculation. xz-plane; first contours respectively ±0·0025 e (a.u.)$^{-3}$; neighbouring contours differ by a factor of 2.

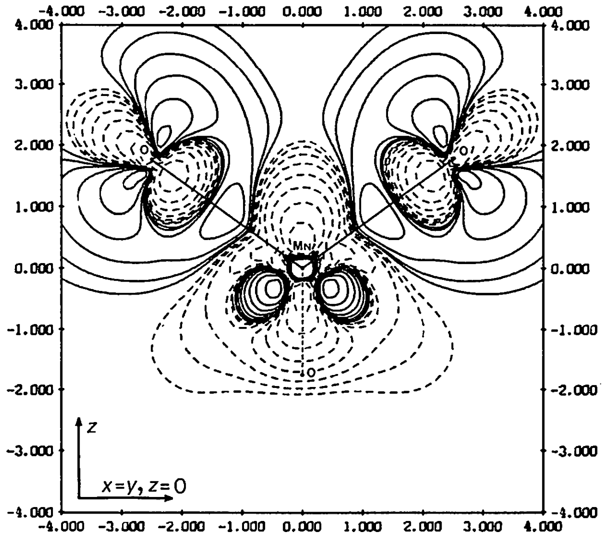

Fig. 3. Deformation density for MnO_4^- in the closed shell $^1A_1$ ground state obtained from a Hartree–Fock type calculation. Abscissa: $z=0, x=y$ and ordinate: $x=0, y=0$; first contours respectively $\pm0{\cdot}0025$ e (a.u.)$^{-3}$; neighbouring contours differ by a factor of 2.

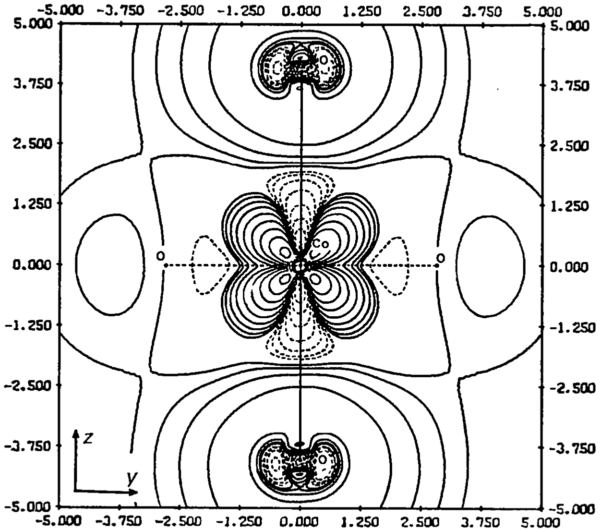

Fig. 4. Deformation density for CoO_6^{10-} in the $^4T_{1g}$ ground state obtained from a limited configuration interaction calculation. yz-plane; first contours respectively $\pm0{\cdot}0025$ e (a.u.)$^{-3}$; neighbouring contours differ by a factor of 2.

peaks close to the metal are observed, on this occasion at distances of 0·25 Å from the Co nucleus and with heights of 4 e Å^{-3}. The excess charge is in the yz and x^2-y^2 orbitals and the deficiency in the xy, xz and z^2 orbitals. In this case the configuration interaction has led to the movement of some charge from the xz to the yz and x^2-y^2 orbitals, so the distribution is somewhat different from that based upon the Hartree–Fock solution.

In all cases the peaks are located in regions where the d orbitals have high density. However, the radial maxima for the d orbitals of Mn, Co and Ni, which occur at distances of 0·41, 0·36 and 0·34 Å respectively (Mann, 1968), do not correlate directly with the distance between each peak maximum and the appropriate central atom. Tentatively, it might be suggested that the peaks around Mn and Co do correlate and that the lack of agreement that then arises in the Ni case is due to deficiencies of the basis set. Further investigations are required to test this hypothesis. The peaks in this theoretical study are located at shorter distances from the metal atoms and are higher than those found in analogous experimental investigations (Rees & Coppens, 1973; Iwata & Saito, 1973; Marumo *et al.*, 1974). The main reason for this discrepancy is probably the inadequate description of the thermal motion. Comparison of this kind should therefore be of a qualitative nature only, and the differences in treatment of thermal motion should always be borne in mind.

Deformation density maps will probably show similar peaks for most transition metal compounds with unfilled d shells. They are in fact analogous to lone-pair densities in that they arise from rather localized orbitals with high occupancy, often close to 2. The localization arises from the fixation of the d orbitals when a molecular or crystalline symmetry is imposed.

Dr K. J. Watson, Dr E. N. Maslen and Professor J. P. Dahl are gratefully acknowledged for discussions. Part of the study was supported by a grant from Statens naturvidenskabelige Forskningsråd, Denmark and computations were performed at NEUCC, The Technical University of Denmark.

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