The Crystal and Molecular Structure of the Mixed-ligand Chelate formed from Nickel(II) Dithizonate and Bipyridyl

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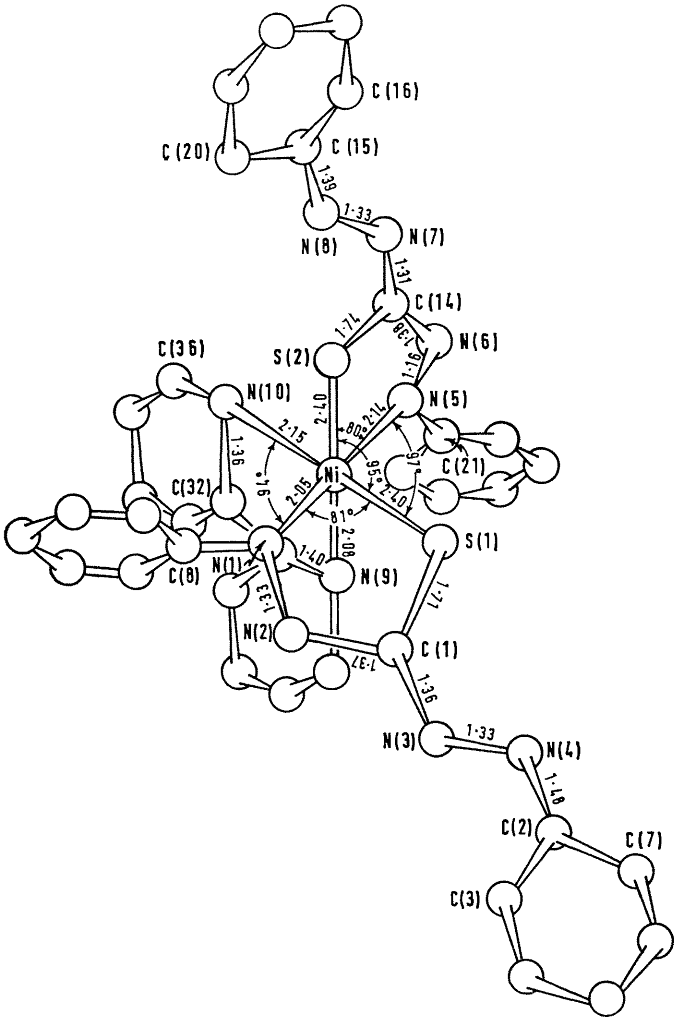
Summary The nature of the metal–ligand bonding, rather than that of the bonding atoms, is responsible for the unique properties of nickel dithizonate.

THE relative insensitivity of nickel to adverse steric effects in formation equilibria involving substituted dithizones (diphenylthiocarbazone) as well as some unusual spectral behaviour of nickel dithizonate[1] cast some doubt on the nature of the bonding atoms involved in the chelate ring. Most metal dithizonates have similar absorption spectra, a single band in the range of 500—550 nm, and are considered to involve one N and one S atom bonded to the metal ion. This structure is confirmed for the Cu^{II} and Hg^{II} chelates by X-ray structure determination.[2,3] The spectrum of nickel dithizonate, on the other hand, is markedly different from that of the other dithizonates, and resembles that observed for the Ni complex of a dithizone-related formazyl,[4] for which a six-membered chelate ring structure involving only nitrogen bonding atoms has been advanced. These observations, as well as the apparent absence of steric hindrance in the stability of the Ni chelate of di-(*o*-tolyl)thiocarbazone, led us to attempt to solve the question of the nature of the bonding atoms in the chelate ring of nickel dithizonate by means of X-ray analysis.



FIGURE

Difficulties with obtaining crystals suitable for X-ray examination led us to test pyridine and other heterocyclic nitrogen solvents and thus to the observation of mixed-ligand chelate formation.[5] Analysis of the absorption spectra of these mixed-ligand chelates enabled us to identify the unique nickel dithizonate spectrum as the result of charge-transfer processes rather than any supposed difference in metal bonding atoms. It was decided that a crystallographic investigation of the mixed ligand chelate of nickel dithizonate and bipyridyl would serve to identify the nature of the bonding atoms in the chelate ring of nickel dithizonate.

Crystals of $NiDz_2$·bipy, which were grown from a benzene solution of nickel dithizonate containing a slight excess of bipyridyl, formed as dark parallelepipeds. The space group was determined by Laue symmetry and systematic absences in the Weissenberg photographs of $h0l$—$h2l$ and $hk0$—$hk2$ reflections. Systematic absences of $0k0$ reflections with k odd and $h0l$ reflections with l odd indicated that the crystals belong to the monoclinic space group $P2_1/c$–C^5_{2h} with cell dimensions $a = 15{\cdot}60 \pm 0{\cdot}02$, $b = 13{\cdot}27 \pm 0{\cdot}02$, $c = 19{\cdot}60 \pm 0{\cdot}02$ Å, and $\beta = 116{\cdot}8°$; D_0 1·32 g/cm³ (flotation), $D_c = 1{\cdot}33$ g/cm³ (assuming $Z = 4$).

Intensity data were obtained using the multiple-film technique with Weissenberg photographs of eight layers taken about the b axis with Ni-filtered Cu-$K\alpha$ radiation. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied. Atomic scattering factors were obtained from the International Tables. A three-dimensional Patterson synthesis was used to obtain the approximate position of the nickel atom. The remaining atoms were located by three successive Fourier syntheses using the complete set of 2026 observed reflections. At this stage the R factor was 0·343. A full-matrix isotropic least-squares refinement of the 49 atoms other than hydrogen in the asymmetric unit gave a value of $R = 0{\cdot}211$. After one cycle of anisotropic refinement which included all of the molecule except for one phenyl ring, the value of R was reduced to 0·136.

Figure 1 gives the main structural features of the molecule. The standard deviations of the interatomic distances are 0·04 Å or less. The four nitrogen and two sulphur bonding atoms lie in an essentially octahedral array about the central nickel atom, at distances within the expected range for a hexaco-ordinated nickel atom. From this it would appear certain that in nickel dithizonate itself, bonding to the metal involves one nitrogen and one sulphur atom, as is the case with other metal dithizonates.

Most of the atoms of the dithizone molecule lie close to the plane of the chelate ring except for the phenyl ring attached to the nitrogen in the chelate ring. Although the position of this almost perpendicular phenyl group may well represent accommodation to the insertion of the bipyridyl, it is likely that it is far out of plane from the chelate ring in simple nickel dithizonate, also. This would be consistent with the unusual absence of any loss of stability of the nickel chelate when this phenyl ring bears an *o*-methyl substituent. Because the corresponding zinc chelate was shown to be less stable than the parent compound, it is interesting to speculate whether, in zinc dithizonate, the phenyl ring attached to the chelate ring is coplanar with it. Bipyridyl and phenanthroline are thus bidentate in their adduct complexes with nickel dithizonate, as we previously assumed.[5]

An interesting feature of the structure of this mixed ligand chelate is the *cis*-position of the two bonding sulphur atoms. It would seem more likely that in nickel dithizonate itself the sulphurs would be *trans*, since this is the case with both the copper[2] and mercury[3] chelates. If so, then one could picture the adduct formation as involving a 90° rotation of the sulphur of one of the dithizonechelate rings about an axis defined by the two dithizone nitrogen bonding atoms. This would indicate that either the Ni–S bond is not as strong as the Ni–N bond or that simply getting the two bulky sulphur atoms out of the way would provide more room (and hence greater stability) for the bipyridyl adducting ligand. Study of adducts of dithizonates of metal ions having greater affinity for sulphur, *e.g.* copper, may resolve this question.

At this stage of refinement it is not possible unequivocally to assign a bond order to the N–N atoms in the chelate ring, although the evidence from bond distances and angles seems to favour the double bond slightly.

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