The Crystal Structure of [Ni(β-picoline)$_2$(NO$_2$)$_2$]$_3$·C$_6$H$_6$: a Linear Trimer with a Novel Nitrite Bridge

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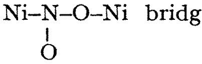
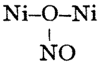
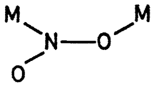
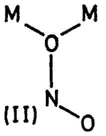
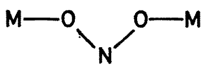
Summary The compound [Ni(β-picoline)$_2$(NO$_2$)$_2$]$_3$·C$_6$H$_6$ is a linear trimer containing three different types of nitrite co-ordination-chelate,  $\mathrm{Ni{-}\underset{\underset{O}{|}}{N}{-}O{-}Ni}$ bridges, and  $\mathrm{Ni{-}\underset{\underset{NO}{|}}{O}{-}Ni}$ bridges.

THE nitrite ion can potentially bridge metal ions in three ways (I, II, and III). Bridges of type (I) are well established, but those of types (II) and (III) are unknown hitherto. The presence of a type (II) bridge was suggested[1] for the compound [Ni en$_2$NO$_2$]ClO$_4$, but it was later shown[2] for the isomorphous fluoroborate salt that the bridge was in fact of type (I). Type (III) bridges were postulated[3] for [Ni en$_2$NO$_2$]X, (X = Cl, Br, and I), but an X-ray study has shown[4] that the nitrite groups chelate in these salts. We report here the preparation, properties, and structure of a novel nickel nitrite compound, [Ni(β-picoline)$_2$(NO$_2$)$_2$]$_3$·C$_6$H$_6$, in which three different types of nitrite co-ordination are present, including, for the first time as far as we are aware, an authentic example of a type (II) nitrite bridge.


(I)


(II)


(III)

The complex was obtained from a solution[5] of Ni(β-picoline)$_4$(ONO)$_2$ in boiling benzene, which, when left to stand for several days in a stoppered flask, deposited dark violet, almost black, monoclinic crystals. Related complexes with pyridine and γ-picoline were obtained by similar methods. These complexes are magnetically non-dilute, displaying Curie–Weiss behaviour of antiferromagnetic sign; the β-picoline complex, for instance, has a θ value of $-76°$. The i.r. spectra of these compounds are notable for the large number of nitrite bands; for the β-picoline complex these are at 1460s, *ca.* 1412s, 1299m, 1236m, 1236vs, 1019s, 863m, and 843m cm.$^{-1}$. The bands below 900 cm.$^{-1}$ are δ(NO$_2$) modes, and the bands at 1236 and 1299 cm.$^{-1}$, and 1236 and 1412 cm.$^{-1}$ are characteristic[6] of chelating and type (I) bridging nitrite groups, respectively. The bands at 1019 and 1460 cm.$^{-1}$ were taken[6] to indicate type (II) bridges. The reflectance spectra of these complexes are also unusual, showing two strong bands in the ν_2 region (at 20,600 and 17,400 cm.$^{-1}$ for the β-picoline complex) as well as a broad ν_1 band at *ca.* 10,600 cm.$^{-1}$. Because of the manner in which the type (I) bridges occur in the trimer (see Figure), the two outer metal ions experience a stronger ligand field than the central one (nitrogen co-ordination of the nitrite ion produces a stronger ligand field than oxygen co-ordination). The observed spectrum is therefore a superposition of the spectra of these two types of nickel ion.

[Ni(β-picoline)$_2$(NO$_2$)$_2$]$_3$·C$_6$H$_6$ has space group $P2_1/c$ and lattice constants $a = 12{\cdot}06$, $b = 16{\cdot}88$, $c = 13{\cdot}28$ Å, and $\beta = 115{\cdot}75°$ with $Z = 2$ units of the above stoicheiometry. There is a rather severe thermal attenuation, so the structure has had to be determined by three-dimensional X-ray techniques on the basis of a mere 829 visually estimated independent reflections; the R factor now stands at 0·125. The structure consists of centrosymmetric *trimeric units* the structure of which is shown in the Figure. (The benzene molecules occur merely as solvates.)

All the atoms in the inorganic sheet (Ni and nitrites) are coplanar to within $\pm 0{\cdot}25$ Å, including the free nitrogen and oxygen of the type (II) nitrite. The participation of a type (II) nitrite *via* oxygen is energetically unlikely and seemingly inconsistent with the observed marked stability of the whole molecule, but there seem to be several compensating sources of stability.

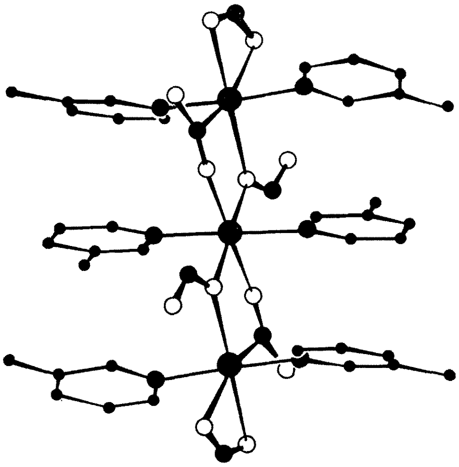


FIGURE. *Diagram of the trimer in* [Ni(β-picoline)$_2$(NO$_2$)$_2$]$_3$.C$_6$H$_6$.

(1) Six-membered rings containing two type (I) nitrites would have been severely buckled and thus devoid of π-conjugation. The five-membered ring found here with non-adjacent metals is novel: though slightly puckered, it is essentially coplanar with the whole of the inorganic sheet, and is thus able to participate in an extended scheme of π-delocalisation throughout this sheet.

(2) The metal atoms are separated by 3·57 Å, just right for putting the six aromatic rings in optimal positions to cohere strongly by dispersion forces and so to stiffen the inorganic sheet. It is significant that apparently similar polymers are formed with pyridine, γ-picoline, and isoquinoline,[6] whereas with aliphatic amines or ammonia which have different steric requirements and cannot provide similar strong cohesive forces, complexes of similar stoicheiometry are formed, but they contain only type (I) nitrite bridges.[6]

In view of these stabilising factors it seems likely that this general structural arrangement may be found in a number of variants.

(*Received, October 16th,* 1969; *Com.* 1569.)

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