A Binuclear Nickel Complex with a Short Nickel–Nickel Bond

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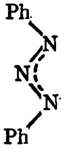
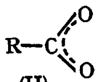
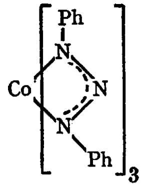
THE anion derived from 1,3-diphenyltriazene (Hdpt) has been likened to the carboxylate family of anions with regard to its co-ordination behaviour.[1] The basis of this comparison is that the geometry of the NNN group[2] of the 1,3-diphenyltriazenido-anion (dpt) (I) closely resembles that of the OCO group[3] of the carboxylate anions (II) in both the free environment and when co-ordinated to transition-metal ions. Both of these systems display bidentate behaviour and two distinct modes of bonding have been observed. The first of these is where both terminal atoms are co-ordinated to the same metal atom to form a four-membered chelate ring; examples[4,5] of this type are found in tris-(1,3-diphenyltriazenido)-cobalt(III)–toluene (IIIa) and zinc(II) acetate dihydrate (IIIb). The other mode of bonding is where the two terminal atoms of the ligands are bonded to two different metal atoms to give a bridged structure. An example of this type is the binuclear complex bis-(1,3-diphenyltriazenido)di-copper(I) (IVa),[6] which has two bidentate ligands bridged between the two metal atoms. Similarly, the substituted carboxylate anion, perfluorobutyrate, exhibits this bridging arrangement in bis(perfluorobutyrate)disilver(I) (IVb).[7]



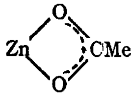
(I)



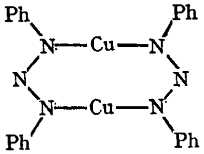
(II)



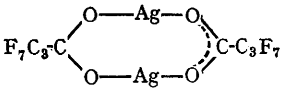
(IIIa)



(IIIb)



(IVa)



(IVb)

The 1,3-diphenyltriazene derivative of Cu^{II}, Ni^{II}, and Pd^{II} are also all binuclear. Considering this, together with the diamagnetic behaviour of the Cu^{II} complex, it was proposed that the structure of these complexes closely resembles that of copper(II) acetate monohydrate.[8] However, spectral studies and the diamagnetic behaviour of the nickel(II) complex were not diagnostic of a metal–metal interaction.[9]

We now report a single crystal *X*-ray study which confirms that tetrakis-(1,3-diphenyltriazenido)dinickel(II) is structurally analogous to copper(II) acetate monohydrate. Significant metal–metal interaction is indicated by the nickel–nickel distance of 2·38 Å which is short compared with the corresponding distance in metallic nickel (2·49 Å),[3] and appreciably shorter than the copper–copper distance (2·64 Å),[8] in copper(II) acetate monohydrate.

1·32 Å and 115·8°, respectively, compare well with previously reported figures as shown in Table.

In the nickel complex the plane of each of the phenyl substituents is skewed considerably with respect to the plane of its triazenido-group in contrast to the copper(I) complex, which is an essentially planar molecule. The mean phenyl-carbon–nitrogen bond length of 1·43 Å is consistent with the value of 1·43 Å given for C(Ar)–N and other published values (Table).[3]

TABLE

Compound	N–N (Å)	N–N–N	N–C (Å)	Ref.
$Ni_2(dpt)_4$	1·32	115·8°	1·43	—
Cu_2dpt_2	1·30	116·0	1·44	6
$Co(dpt)_3$	1·31	(105·0)	1·39	4
$[Cu(dmt)]_4$	1·29	116·0	1·50	12
dpt,H,Br_2	1·24	113·0	1·45	2

dmt = 1,3-dimethyltriazenido anion.

Crystal data for tetrakis(1,3-diphenyltriazenido)dinickel(II) ($C_{48}H_{40}N_{12}Ni_2$); $M = 902\cdot3$, triclinic, $a = 10\cdot3_7$, $b = 15\cdot9_1$, $c = 13\cdot5_3$ Å; $\alpha = 99\cdot8_8$, $\beta = 93\cdot5_2$, $\gamma = 103\cdot1_3$°; $D_m = 1\cdot41$, $Z = 2$, $D_c = 1\cdot40$ g.cm.$^{-3}$; space group $P\bar{1}$ (C_i^1, No. 2), Cu (unfiltered) radiation, single-crystal oscillation and equi-inclination Weissenberg photographs.

From the three-dimensional Patterson function (computed using 3300 independent reflections) the two unique nickel atoms were located. The subsequent heavy-atom phased Fourier syntheses enabled the other sixty atoms of the asymmetric unit (*i.e.* all atoms excluding the hydrogen atoms) to be located. Refinement was carried out by the method of least squares. The present value of the reliability index R is 0·14, based on observed reflections only and isotropic temperature factors.

The crystals of tetrakis(1,3-diphenyltriazenido)dinickel(II) are composed of discrete molecules of composition $Ni_2(dpt)_4$. In each molecule, the nickel atoms are bridged by four ligand groups bonded through the terminal nitrogen atoms as shown in the Figure. The bonded nitrogen atoms are disposed about the metal atoms in two square planar arrays; the planes being superposed and parallel. The nickel atoms are situated in the centres of the two planes. In relation to either square plane, the neighbouring nickel atom lies at the apex of a right square pyramid base on that plane.

The nickel–nitrogen bond lengths are all nearly equal, the average being 1·93 Å. This value agrees favourably with other published values.[3] There appear to be no significant differences in the nitrogen–nitrogen distances which suggests some delocalization of π-electrons over the triazenido-moiety of the complex. The average value of the N–N bond lengths and the N–N–N angles of

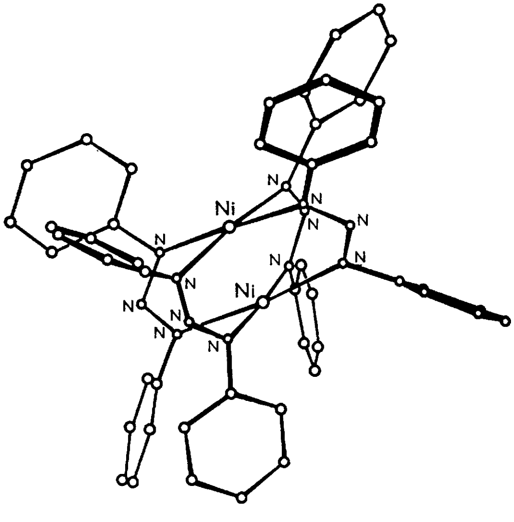


FIGURE. *The* $Ni_2(dpt)_4$ *molecule viewed down the* a *axis.*

Close metal–metal distances have been reported for the two nickel compounds, bis(dimethylglyoxime)nickel(II)[10] and the trimeric complex bis(acetylacetonato)nickel(II)[11] where the nickel–nickel distances are 3·25 and 2·89 Å respectively. The metal–metal distance of 2·38 Å in tetrakis(1,3-diphenyltriazenido)dinickel(II) appears, to our knowledge, the shortest reported in any nickel(II) complex.

We thank Dr. J. C. B. White, Dr. D. A. Wright, and Mr. S. A. Mason for the use of their computer programmes.

(*Received, October 10th*, 1968; *Com.* 1376.)

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