756. *The Nature of the Metal Complexes of* 1,3-*Diphenyltriazen.*

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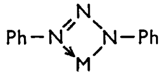
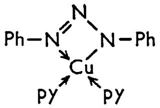
The bivalent copper and palladium complexes of 1,3-diphenyltriazen (dpth) have been shown to exist as dimers (M_2 dpt$_4$) (M = Cu and Pd), in solvents such as benzene and nitrobenzene. The copper complex is diamagnetic, both in solution and in the solid state, and it is suggested that these compounds, as well as the analogous nickel complex, possess a bridged structure similar to that of copper(II) acetate. The diamagnetic nickel compound [Ni_2 dpt$_4$] forms paramagnetic (μ ~3·2 B.M.) adducts Ni dpt$_2$ py$_2$ and Ni dpt$_2$ phen with pyridine and 1,10-phenanthroline.

Quadricovalent palladium(II) complexes, Pd dpt$_2$ dpth$_2$, $PdCl_2$ dpth$_2$, and Pd dpt$_2$ phen, in which 1,3-diphenyltriazen and its derived anion function as unidentate groups, have also been prepared and examined.

It has long been known that various metals can displace the imino-hydrogen atom from 1,3-diphenyltriazen (diazoaminobenzene), and it has been suggested that both the parent "acid" (dpth) and the derived anion (dpt) function as bidentate chelating groups.[1,2] Dwyer[1] concluded that in the lemon-yellow silver(I) complex[3] Ag(dpt) the silver atom is co-ordinately saturated and that both this compound and the analogous copper(I) derivative[4] have structure (I). The dipyridine adduct Cu dpt py$_2$ was formulated as in (II).[1]

Bivalent metal complexes of the empirical formula M dpt$_2$ (where M = Cu,[1,4,5] Ni,[2] Pd,[1] and Hg[5-8]) have also been isolated. The copper and palladium complexes were assigned the uninuclear square-co-ordinated structure (III) on the basis of ebullioscopic molecular-weight measurements,[1] whereas the diamagnetic nickel compound was assigned structure (IV) because of its dimerism in freezing benzene.[2]


(I)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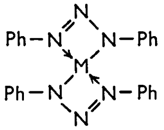
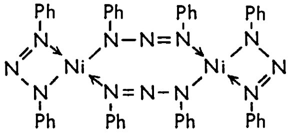

M = Cu(II) or Pd(II)

(III)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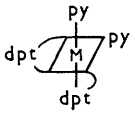
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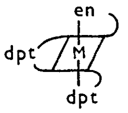
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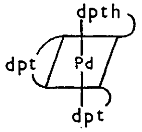
(VII)

In addition to the above bivalent metal complexes, the compounds M dpt$_2$ py$_2$ and M dpt$_2$ en (where M = Cu, Ni, or Pd, py = pyridine, and en = ethylenediamine) have also been described,[1,2] as well as an unstable palladium complex formulated as Pd dpt$_2$ dpth.[1] The palladium and nickel compounds have been assigned the sexicovalent structures (V—VII) in which the triazen molecule and its derived anion function as bidentate chelate

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[1] Dwyer, *J. Amer. Chem. Soc.*, 1941, **63**, 78.

[2] Dwyer and Mellor, *ibid.*, p. 81.

[3] Griess, *Annalen*, 1862, **121**, 261; 1866, **137**, 53; see also ref. 8 and Meunier and Rigot, *Bull. Soc. chim. France*, 1900, **23**, 104.

[4] Meunier, *Compt. rend.*, 1900, **131**, 52; see also Niementowski and Roszkowski, *Z. phys. Chem.*, 1897, **22**, 145.

[5] Mangini and Dezudicibus, *Gazzetta*, 1933, **63**, 601.

[6] Cuisa and Pestalozza, *ibid.*, 1911, **41**, I, 394; *Atti R. Accad. Lincei*, 1911, **18**, II, 90.

[7] Veichiotte and Capondacqua, *Gazzetta*, 1925, **55**, 369.

[8] Watt and Fernelius, *Z. anorg. Chem.*, 1934, **221**, 187.

groups. Finally it may be noted that bivalent mercury forms both a bis-complex Hg dpt_2[2,5-8] as well as the dichloro-complex $HgCl_2$ $dpth_2$.[9-11]

The structures so far proposed for these metal–triazen complexes in general involve this ligand in a four-membered ring which might be expected, from a consideration of the valency angles, to be considerably strained. However, the palladium(II) and nickel(II) complexes are exceptionally stable and markedly indifferent to strongly co-ordinating ligands such as pyridine and ethylenediamine. Hence, it appears that the proposed structures are not completely compatible with the properties of these compounds and this fact coupled with their importance as accepted examples of four-membered chelate rings has led us to re-investigate their properties.

TABLE 1. *Metal complexes of* 1,3-*diphenyltriazen* (dpth).

Metal	Empirical formula	Colour	Molecular formula
Cu(I)	Cu dpt	Yellow or orange	Probably polymeric
Ag(I)	Ag dpt	Yellow	Probably polymeric
Cu(II)	Cu dpt_2	Dark-green	Cu_2 dpt_4
			Cu_2 dpt_4, CH_3OH *
Ni(II)	Ni dpt_2	Red	Ni_2 dpt_4
	Ni dpt_2 py_2	Yellow-brown	Probably polymeric
	Ni dpt_2 phen	,,	Probably polymeric *
Pd(II)	Pd dpt_2	Dark-brown	Pd_2 dpt_4
		,,	Pd_2 dpt_4, $0{\cdot}5C_6H_6$ *
		,,	Pd_2 dpt_4, $CH_3{\cdot}CO{\cdot}CH_3$ *
	$PdCl_2$ $dpth_2$	Orange-brown	$PdCl_2$ $dpth_2$, $0{\cdot}5CH_3{\cdot}CO{\cdot}CH_3$ *
	Pd dpt_2 $dpth_2$	Reddish-brown	Pd dpt_2 $dpth_2$,H_2O *
		,,	Pd dpt_2 $dpth_2$,$0{\cdot}5CH_3OH$ *
	Pd dpt_2 py_2	Orange	Pd dpt_2 py_2,C_5H_5N *
		,,	Pd dpt_2 py_2,C_6H_6 *
	Pd dpt_2 phen	Orange-brown	Pd dpt_2 phen *
		,,	Pd dpt_2 phen,$0{\cdot}5C_6H_6$ *
Hg(II)	Hg dpt_2	Yellow	Probably polymeric
	$HgCl_2$ $dpth_2$	,,	Probably polymeric

* These compounds are reported here for the first time.

TABLE 2. *Molecular weight of metal triazen complexes.*

Mol. formula	Method (all in C_6H_6)	Concn. (g./100 g.)	ΔT	Mol. wt. obs.	Mol. wt. calc.
Cu_2 dpt_4	Cryosc.	0·39	0·021°	920	
		0·46	0·019	1180	
		0·39	0·020	960	910
	Ebull.[1]	1·35	0·038	930	
		0·91	0·023	1030	
Ni_2 dpt_4	Cryosc.	0·21	0·012	980	
	Ebull.	0·47	0·011	1100	900
Pd_2 dpt_4	Cryosc. $PhNO_2$	0·15	0·009	1160	
		0·12	0·007	1160	998
	Ebulliosc.	0·78	0·020	1020	
Pd dpt_2 $dpth_2$	Cryosc.[2]	0·22	0·031	780	
		0·43	0·055	825	893
Pd dpt_2 py_2	Cryosc.[3]	0·47	0·047	555	
		0·17	0·020	480	656

[1] In the ebullioscopic determinations, the green solution of the copper(II) complex decomposes with the formation of orange products after some minutes, and the b. p. slowly rises. B. p. elevations observed over the first 5 min., on the green solution, correspond to the dimeric formula.

[2] This compound was used as hydrate, in the presence of Na_2SO_4–$Na_2SO_4,10H_2O$.

[3] This compound was used as solvate containing 1 mol. of benzene.

The complexes of 1,3-diphenyltriazen with copper, nickel, palladium, silver, and mercury, which have been prepared and examined during this investigation, are listed in Table 1. The copper(II), nickel(II), and palladium(II) complexes of empirical formula M dpt_2 are listed as dimers on the basis of molecular-weight measurements (see Table 2).

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[9] Hantzsch and Perkin, *Ber.*, 1897, **30**, 1412.

[10] Mandal, *Science and Culture*, 1940, **6**, 59.

[11] Knowles and Watt, *J. Amer. Chem. Soc.*, 1942, **64**, 935.

Many of the compounds displayed a marked tendency to crystallise with solvent of crystallisation which in some cases was not removed by heating them at reduced pressures. These compounds are all diamagnetic, with the exception of several of the nickel complexes whose magnetic moments are listed in Table 3.

The preparation and properties of the compounds in Table 1 are briefly outlined below, in order to contrast them with previous results, which in a number of cases are at variance with ours.

Copper(I) *and Silver*(I).—The copper and silver compounds of the type M dpt were prepared by Dwyer's method,[1] but were not sufficiently soluble in solvents other than pyridine for molecular-weight measurements. Although the copper(I) compound has been reported to be monomeric in boiling benzene,[1] we have been unable to repeat this measurement since the compound is not sufficiently soluble. Attempts to measure the molecular weight in camphor also failed owing to decomposition.

The silver compound has been reported to be monomeric in pyridine; [1] this, however, is a strong donor solvent which could be co-ordinated to the silver atom in solution. The compound is not sufficiently soluble in non-donor solvents for molecular-weight determinations.

Copper(II).—The dark green copper(II) complex was prepared as the solvate Cu_2 dpt_4, MeOH by treating copper(II) acetate with the ligand in methanol. The solvent-free complex was obtained by reprecipitating the compound from benzene with light petroleum. In the present work this compound has been shown to be dimeric from molecular-weight measurements in freezing benzene. The compound had been previously formulated [1] as the monomer on the basis of molecular complexities in bromoform as high as 1·5.

TABLE 3. *Magnetic susceptibility of metal–triazen complexes.*

Compound	Temp. (K)	$10^6\chi_g$	$10^6\Delta$ *	$10^6\chi_M$	μ (B.M.)
Cu_2 dpt_4	91°	0·14	−154	+281	0
	294	0·09	−154	+236	0
	359	0·12	−154	+263	0
Ni_2 dpt_4	294	−0·112	−156	+55	0
Ni dpt_2 py_2	300	6·91	−189	+4394	3·25
Ni dpt_2 phen	292	6·67	−207	+4417	3·23
Pd_2 dpt_4	294	—	—	Diamagn.‡	0
Pd dpt_2 $dpth_2$	294	−0·38	−157	−171	0
dpth	299	−0·167	—	−33	0
Cu_2 dpt_4 (benzene soln.†) (0·00685M)	294	−0·2	−154	Diamagn.	0

* Including diamagnetic correction for M^{++}. † Method as described by Martin and Whitley.[13]
‡ Insufficient for quantitative measurement.

Although this compound is diamagnetic, as is the above copper(I) complex, the absorption spectra of the copper(II) and copper(I) complexes are markedly different in the visible region. The copper(II) compound is characterised by a broad and unsymmetrical absorption maximum centred at ~625 mμ with ε 1850. Nitrogen-linked copper(II) complexes are well known to possess a broad absorption band in this region, although the extinction coefficients for these compounds are considerably lower.

Unlike the nickel(II) and palladium(II) derivatives discussed below, this compound is unstable in hot solvents, and presumably undergoes rapid self-reduction to orange-brown solutions of the copper(I) complex, as suggested by Dwyer.[1] Attempts to prepare the reported [1] indigo-blue dipyridine adduct Cu dpt_2 py_2 were unsuccessful, apparently owing to reduction of the compound.

Nickel(II).—The dipyridine compound, Ni dpt_2 py_2, was obtained by Dwyer's method,[2] and shown to be paramagnetic with a moment of $\mu = 3·2$ B.M./Ni atom, corresponding to the presence of two unpaired electrons. It was found that this paramagnetic complex was readily converted, in refluxing toluene, into the red diamagnetic binuclear compound Ni_2 dpt_4. This compound had been prepared [2] by heating the solid dipyridine complex at 120—130° for 15 hours. A paramagnetic ($\mu = 3·2$ B.M./Ni atom) 1,10-phenanthroline complex, Ni dpt$_2$ phen, was obtained by refluxing the diamagnetic dimer with 1,10-phenanthroline in benzene. The molecular weight of the dimer was confirmed cryoscopically in benzene (see Table 2); the pyridine and phenanthroline derivatives were too insoluble for cryoscopic molecular-weight determinations.

Palladium(II).—On attempting to prepare the compound previously reported[1] as impure Pd dpt$_2$ dpth, we obtained the compound Pd dpt$_2$ dpth$_2$,H$_2$O. The water was readily replaced by half a molecule of methanol. This compound is monomeric in freezing benzene in the presence of sodium sulphate. When the compound is refluxed in acetone, it dissociates, forming the dimer, Pd$_2$ dpt$_4$,COMe$_2$. On precipitation from benzene with light petroleum, the acetone was replaced and the compound Pd$_2$ dpt$_4$,0·5C$_6$H$_6$ was obtained from which the benzene was removed at 180°. The solvent-free compound was shown to be binuclear by both cryoscopic and ebullioscopic molecular-weight measurements (see Table 2).

The orange crystalline compound, Pd dpt$_2$ py$_2$, py, was prepared by dissolving Pd dpt$_2$ dpth$_2$ in pyridine and precipitating the new compound by water. On dissolution of this compound in benzene and precipitation with light petroleum, the lattice pyridine was replaced by benzene. The benzene was not removed *in vacuo* at 100°. The compound is monomeric in benzene at the freezing point (see Table 2).

The 1,10-phenanthroline complex, Pd dpt$_2$ phen,0·5C$_6$H$_6$, was obtained by treating Pd dpt$_2$ dpth$_2$ with phenanthroline in warm benzene. The benzene was removed at 100° *in vacuo*. The dichloro-complex PdCl$_2$ dpth$_2$,0·5COMe$_2$ was also obtained by mixing potassium tetrachloropalladate(II) with diphenyltriazen in 50% aqueous acetone. This compound and the above phenanthroline complex were not sufficiently soluble for molecular-weight measurements.

EXPERIMENTAL

1,3-*Diphenyltriazen*.—Diazoaminobenzene (from British Drug Houses Ltd.) was purified by repeated recrystallisation from 50% ethanol containing a small amount of potassium hydroxide and carbon. It had m. p. 99—100° (Found: C, 72·9; H, 5·4; N, 21·2. Calc. for $C_{12}H_{11}N_3$: C, 73·1; H, 5·6; N, 21·3%).

Dichlorobis(1,3-*diphenyltriazen*)*palladium*(II).—A solution of 1,3-diphenyltriazen (0·5 g.) in 50% acetone (150 ml.) was added slowly with stirring to a 50% acetone solution (50 ml.) of potassium tetrachloropalladate (0·33 g.). The orange-brown *compound* which was deposited was filtered off, washed with 50% acetone, and dried at 100° (Found: C, 51·8; H, 4·0; N, 14·5; Cl, 11·9; Pd, 17·9. $C_{24}H_{22}N_6Cl_2Pd,0{\cdot}5C_3H_6O$ requires C, 51·0; H, 4·2; N, 14·0; Cl, 11·8; Pd, 17·7%). The acetone of crystallisation was not lost at 100°.

Bis-(1,3-*diphenyltriazenido*)*bis*-(1,3-*diphenyltriazen*)*palladium*(II).—This compound was prepared by dropwise addition of an ice-cold mixture of aqueous potassium tetrachloropalladate (3·3 g./35 ml.) and 3N-sodium acetate (15 ml.) to a chilled methanolic solution of the triazen (12 g./200 ml.). Almost immediately, reddish-brown crystals were deposited. The *compound* was filtered off, washed with ice-cold (80%) methanol, and dried *in vacuo* (P_2O_5) (Found: C, 62·9; H, 4·6; N, 18·1; Pd, 12·0. $C_{48}H_{42}N_{12}Pd,H_2O$ requires C, 63·3; H, 4·9; N, 18·5; Pd, 11·7%). When this compound is dissolved in cold benzene and precipitated by a large excess of cold methanol the lattice water is replaced by 0·5 mole of methanol (Found: C, 64·0; H, 4·7; N, 18·0; Pd, 11·8. $C_{48}H_{42}N_{12}Pd,0{\cdot}5CH_3OH$ requires C, 64·0; H, 4·9; N, 18·5; Pd, 11·7%). This *methanolate* was extremely soluble in acetone, benzene, and nitrobenzene, and in acetone or benzene, particularly when heated, readily rearranged and gave a precipitate of $\mu\mu'\mu''\mu'''$-tetrakis-(1,3-diphenyltriazenido)dipalladium(II).

$\mu\mu'\mu''\mu'''$-*Tetrakis*-(1,3-*diphenyltriazenido*)*dipalladium*(II).—The compound bis-(1,3-diphenyltriazenido)bis-(1,3-diphenyltriazen)palladium(II) was refluxed in acetone for some time. The reddish-brown solution became dark brown, and a dark brown crystalline *product* was deposited (Found: Pd, 20·2, 20·4. $C_{48}H_{40}N_{12}Pd_2,C_3H_6O$ requires Pd, 20·2%). Dissolution of this acetone solvate in benzene and precipitation by addition of light petroleum gave a dark brown *compound* (Found: C, 58·4; H, 3·9; N, 16·5; Pd, 20·4. $C_{48}H_{40}N_{12}Pd_2,0{\cdot}5C_6H_6$ requires C, 59·1; H, 4·2; N, 16·2; Pd, 20·5%). The benzene was lost at 180° in 6 hr., giving the unsolvated *compound* (Found: C, 57·5; H, 3·8; N, 16·4; Pd, 21·5. $C_{48}H_{40}N_{12}Pd_2$ requires C, 57·8; H, 4·0; N, 16·9; Pd, 21·4%). This compound was sparingly soluble in most organic solvents, but insoluble in methanol and ethanol.

Bis-(1,3-*diphenyltriazenido*)*dipyridinepalladium*(II).—This was obtained as orange crystals containing a molecule of pyridine of crystallisation by the following method. Bis-(1,3-diphenyltriazenido)bis-(1,3-diphenyltriazen)palladium(II) was dissolved in cold pyridine, and the product precipitated by the addition of water. The orange crystals were reprecipitated three times from pyridine with water. The *compound* was dried over phosphoric oxide (Found: C, 63·8; H, 4·7; N, 16·7; Pd, 14·0. $C_{34}H_{30}N_8Pd,C_5H_5N$ requires C, 63·7; H, 4·8; N, 17·1; Pd, 14·4%). The lattice pyridine was replaced by benzene on dissolving this compound in benzene and precipitating the new solvate by light petroleum (Found: C, 64·8; H, 4·7; N, 15·2; Pd, 14·1. $C_{34}H_{30}N_8Pd,C_6H_6$ requires C, 65·3; H, 4·9; N, 15·3; Pd, 14·4%). The benzene was not lost at 100° *in vacuo* in 1 hr.

Bis-(1,3-*diphenyltriazenido*)-1,10-*phenanthrolinepalladium*(II).—Orange-brown crystals were obtained by treating Pd $dpth_2$ dpt_2 (0·47 g.) with 1,10-phenanthroline monohydrate (0·09 g.) in warm benzene. The *product* was filtered off and crystallised from benzene by addition of light petroleum (Found: C, 64·6; H, 4·2; N, 15·1; Pd, 14·9. $C_{36}H_{28}N_8Pd,0{\cdot}5C_6H_6$ requires C, 65·2; H, 4·4; N, 15·6; Pd, 14·8%). The benzene was removed at 100° *in vacuo* (Found: C, 63·9; H, 4·0; N, 15·9; Pd, 15·7. $C_{24}H_{28}N_8Pd$ requires C, 63·8; H, 4·2; N, 16·5; Pd, 15·7%). The solvent-free *compound* was slightly soluble in benzene and sparingly soluble in nitrobenzene.

Bis-(1,3-*diphenyltriazenido*)*dipyridinenickel*(II).—This compound was prepared by Dwyer and Mellor's method[2] (Found: C, 67·1; H, 4·8; N, 18·2; Ni, 9·5. Calc. for $C_{34}H_{30}N_8Ni$: C, 67·0; H, 4·9; N, 18·4; Ni, 9·6%).

$\mu\mu'\mu''\mu'''$-*Tetrakis-*(1,3-*diphenyltriazenido*)*dinickel*(II).—This compound can be prepared by the method of Dwyer and Mellor,[2] heating the solid dipyridine complex at 120—130° for 10—15 hr. It is readily prepared by refluxing the dipyridine complex in toluene for 3 hr. The red solution was cooled, treated with an equal amount of light petroleum, and kept at 0° for some time. The red crystals were recrystallised twice from benzene solution by addition of alcohol and dried *in vacuo* (Found: C, 64·4; H, 4·4; N, 18·1; Ni, 12·9. Calc. for $C_{48}H_{40}N_{12}Ni_2$: C, 63·9; H, 4·5; N, 18·6; Ni, 13·0%). This compound was moderately soluble in benzene, toluene, and nitrobenzene, but insoluble in acetone, methanol, and ethanol.

Bis-(1,3-*diphenyltriazenido*)-1,10-*phenanthrolinenickel*(II).—A benzene solution of $Ni_2\,dpt_4$ (0·5 g. in 15 ml.) was refluxed with excess of 1,10-phenanthroline monohydrate (*ca.* 0·5 g.) for ~4 hr., the colour changing from deep-red to dark brown, and brown crystals separating. The *product* recrystallised from a large volume of benzene (Found: N, 17·4; Ni, 9·3. $C_{36}H_{28}N_8Ni$ requires N, 17·7; Ni, 9·3%); it was only slightly soluble in benzene and nitrobenzene, and completely insoluble in methanol or ethanol.

$\mu\mu'\mu''\mu'''$-*Tetrakis-*(1,3-*diphenyltriazenido*)*copper*(II).—This was prepared by treating copper(II) acetate monohydrate with a methanolic solution of the ligand, by Dwyer's method.[1] The dark green crystalline compound was washed with ice-cold methanol and dried *in vacuo* over phosphoric oxide. The analytical figures on four separate preparations indicated the presence of one molecule of either methanol or water (in the lattice) which was not removed at 100°/1 mm. (Found: C, 62·2; H, 4·3; N, 18·1; Cu, 13·8. $C_{48}H_{40}N_{12}Cu_2,CH_3{\cdot}OH$ requires C, 62·3; H, 4·7; N, 17·8; Cu, 13·5. $C_{48}H_{40}N_{12}Cu_2,H_2O$ requires C, 61·9; H, 4·6; N, 18·1; Cu, 13·7%). The solvent-free *dimer* was obtained by dissolving the above solvate in cold benzene and precipitating it by light petroleum (Found: C, 63·2; H, 4·5; N, 18·3. Calc. for $C_{48}H_{40}N_{12}Cu_2$: C, 63·2; H, 4·4; N, 18·4%). This was soluble in benzene and nitrobenzene, practically insoluble in methanol and ethanol, and very soluble in pyridine in which it rapidly decomposes.

1,3-*Diphenyltriazenidocopper*(I).—This was prepared by Dwyer's method,[1] with copper(I) iodide in place of copper(I) chloride. The lemon-yellow dipyridine complex was recrystallised twice from pyridine. The pyridine was then removed at 100° in 6 hr. (Found: C, 54·9; H, 3·9; N, 16·4; Cu, 24·3. Calc. for $C_{12}H_{10}N_3Cu$: C, 55·5; H, 3·9; N, 16·2; Cu, 24·5%). The compound was very sparingly soluble in benzene, toluene, acetone, nitrobenzene, and methyl and ethyl alcohol, but extremely soluble in pyridine.

1,3-*Diphenyltriazenidosilver*(I).—This compound was prepared by Dwyer's method[1] and recrystallised from pyridine–methanol (Found: C, 47·6; H, 3·2; N, 13·9; Ag, 35·4. Calc. for $C_{12}H_{10}N_3Ag$: C, 47·4; H, 3·3; N, 13·8; Ag, 35·5%). It was very sparingly soluble in benzene, nitrobenzene, nitromethane, and methyl cyanide although it dissolved readily in hot pyridine.

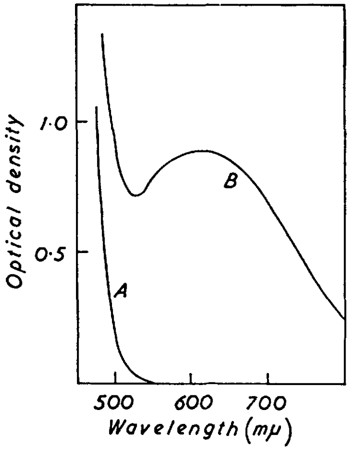
Bis-(1,3-*diphenyltriazenido*)*mercury*(II).—The bis-complex was prepared by treating mercuric acetate with the ligand in ethanol solution. It was purified by dissolution in pyridine–benzene (1 : 20) and precipitation by ethanol. The canary-yellow product was dried at 100° (Found: C, 48·5; H, 3·6; N, 14·3; Hg, 33·8. Calc. for $C_{24}H_{20}N_6Hg$: C, 48·6; H, 3·4; N, 14·2; Hg, 33·8%).

Dichlorobis-(1,3-*diphenyltriazene*)*mercury*(II).—An ethanolic solution of the ligand was added to a solution of mercury(II) chloride (0·69 g.) in alcohol. The orange precipitate was recrystallised from benzene by addition of light petroleum, and the orange-brown compound dried *in vacuo* (Found: C, 43·4; H, 3·1; N, 12·7. Calc. for $C_{24}H_{22}N_6Cl_2Hg$: C, 43·3; H, 3·3; N, 12·6%).

Molecular-weight Determinations.—Cryoscopic measurements were made by the conventional Beckmann method in the presence of 1—2 g. of sodium sulphate, containing a small amount of the decahydrate (see Robertson and Bury [12]) in order to keep a constant vapour pressure of water in both the benzene and the nitrobenzene solution. In a number of cases the determinations were also made in an enclosed moisture-free atmosphere in the all-glass cryoscope described elsewhere.[13] The experimental values quoted in Table 2 are sufficiently accurate to leave no doubt as to whether a compound is mono- or di-meric. However, when the observed depressions are small, the molecular weight values are probably not more accurate than *ca.* ±20%. The ebulliometer used for molecular-weight determinations in boiling benzene was adapted from the design of Sucharda and Bobranski.[14]

Magnetic Measurements.—These were made on powdered samples, by the Gouy method in conjunction with a cryostat cooled by liquid nitrogen. The gram susceptibility χ_g, the molar susceptibility χ_M (corrected for the underlying diamagnetism of all atoms, Δ), and the magnetic moment μ, are set out in Table 3. The magnetic moment is calculated on the basis of a simple Curie law, $\mu = 2{\cdot}839[\chi_M T]^{0\cdot5}$.

Electrical Conductivity.—The electrical conductivity of the above metal triazens, in nitro-benzene solution, was measured at room temperature by means of a Philips A. C. Wheatstone bridge (type G.M. 4249). The measurements were made at a 1000 c./sec., a Philips immersion cell (type G.M. 4221) with platinised electrodes being used. All the compounds were found to be non-electrolytes possessing molecular conductivities less than 0·1 mho at concentrations of $\sim 10^{-3}$molar.



Visible spectra for Cu dpt (*A*) *and* Cu_2 dpt_4 (*B*) *in benzene solution* (M/2000) (1 *cm. cell*).

Absorption Spectra in the Visible Region.—The absorption spectra of both copper complexes Cu dpt and Cu_2 dpt_4 and that of 1,3-diphenyltriazen in benzene solution were recorded between 4000 and 8000 Å, a Cary recording spectrophotometer (Model 11MS-50) being used. The two spectra are illustrated (the ligand did not absorb in this range).

DISCUSSION

In view of the dimeric nature of the copper, nickel, and palladium complexes M_2 dpt_4, and the diamagnetism of the copper(II) complex, it is important to consider the possible bonding modes of the diphenyltriazenide anion and their structural implications.

Recent work with copper(II) acetate is relevant. Lowry and French [15] first postulated that the acetate group functioned as a bidentate chelate, giving the 4-membered ring structure (VIII), but Sidgwick [16] criticized this on the grounds of considerable steric strain and distortion of natural valency angles. Even so, this structure continued to find favour until it was invalidated by the *X*-ray structure demonstration (Niekerk and

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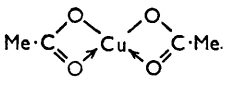
[12] Robertson and Bury, *J.*, 1923, **123**, 2037.
[13] Martin and Whitley, *J.*, 1958, 1394.
[14] Sucharda and Bobranski, *Chem. Ztg.*, 1927, **51**, 568.
[15] Lowry and French, *Proc. Roy. Soc.*, 1924, *A*, **106**, 489.
[16] Sidgwick, " The Electronic Theory of Valency," Oxford University Press, 1927, p. 253.

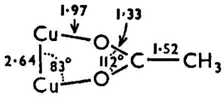
Schoening[17]) that the monohydrate was binuclear $[Cu(CH_3{\cdot}CO_2)_4(H_2O)_2]$, the pairs of contiguous copper atoms (Cu–Cu = 2·64 Å) being supported by four bridging acetate groups whose planes are at right angles. The molecular geometry is based on the 5-membered ring (IX), so that steric strain is eliminated.

Although the structure of 1,3-diphenyltriazene is unknown, it will be apparent from diagrams (X) and (XI) that the geometry of the carboxy-group in fatty acids, which is based on sp^2-hybridisation of the C atom, is likely to parallel closely that of the N_3H group in diphenyltriazen. Further, the three potential bonding modes (XII—XIV) [based on (XI)] are possible if we assume that each diphenyltriazenide anion is bound to two metal atoms.

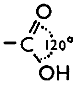
A molecular structure based on the *syn–syn*-bonding arrangement (XII) would lead to close approach of the two copper atoms, and the magnetic moment of the copper atoms could well be modified. In fact, the compound bis-(1,3-diphenylditriazenido)copper(II) has recently[18] been shown to be diamagnetic both in the solid state (between 80° and 400° K) and in benzene solution (at 20° C). Although, the observed diamagnetism in the solid state could conceivably arise from intermolecular Cu–Cu interactions, it is clear that, in benzene solution, intramolecular exchange interaction between copper atoms must occur to a degree sufficient for complete pairing of the unpaired electron associated with the $3d^9$-configuration of each bivalent copper atom. The exchange demagnetisation must arise from the presence of a direct Cu–Cu covalent bond in the dimeric molecule, Cu_2 dpt_4 for which we propose the structure (XV) based on *syn–syn*-bonding. Molecular models confirm that the eight phenyl groups, when suitably orientated, can be accommodated without steric hindrance, but that the terminal positions at each copper atom are not accessible for donor ligands. The observed diamagnetism is unique for copper(II) compounds at room temperature. We now believe the dimeric and diamagnetic nickel and palladium compounds Ni_2 dpt_4 and Pd_2 dpt_4 possess similar binuclear bridged structures, but that their diamagnetism is not diagnostic for the presence of metal–metal interaction since square-co-ordinated nickel(II) and palladium(II) complexes are invariably diamagnetic.



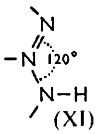
(VIII)



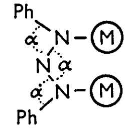
(IX)



(X)

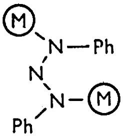


(XI)



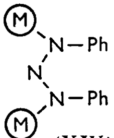
(XII)

Bridge: *syn–syn*



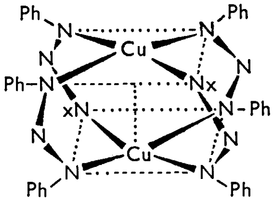
(XIII)

anti–syn



(XIV)

anti–anti



(XV) (x = Ph)

In contrast to the bridged Cu(II) complex, which tends to decompose in hot solvents, the nickel(II) and palladium(II) complexes are thermally rather stable, in the solid state and in solution. Further, the nickel and palladium complexes are comparatively inert to donor solvents such as pyridine, from which they recrystallise unchanged. The nickel complex Ni_2 dpt_4 can be converted into the dipyridine derivative Ni dpt_2 py_2 by prolonged boiling in pyridine. This is compatible with a binuclear structure similar to (XV) in that access to the metal atom is sterically hindered by phenyl groups.

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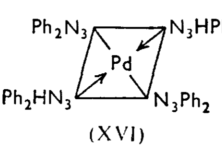
[17] Niekerk and Schoening, *Acta, Cryst.*, 1953, **6**, 227.

[18] Harris and Martin, *Proc. Chem. Soc.*, 1958, 259.

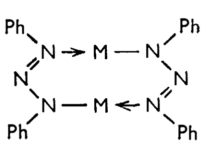
It is worth noting in connexion with the preparation of these complexes that the method of preparation of the copper(II) compound involves direct replacement of acetate bridges in binuclear $Cu_2(CH_3{\cdot}CO_2)_4$ by the triazen in methanol solution. Further, the binuclear nickel(II) complex cannot be obtained in this manner since binuclear nickel(II) acetate is unknown.

It remains to discuss the possible structures of the remaining metal–triazen complexes whose structures cannot be as readily inferred as those of the above bridged compounds. The triazen ligand need not necessarily function as a bridge between two metal atoms as in (XII—XIV) but can conceivably function as a neutral or negatively charged unidentate group.

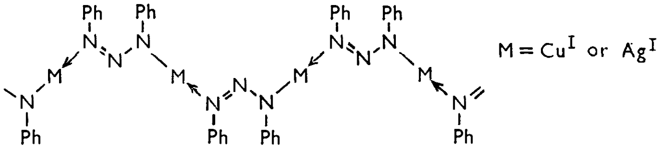
In the case of palladium(II), the unstable and impure compound Pd dpt_2 dpth was postulated to have probably an octahedrally co-ordinated palladium(II) atom, the triazen functioning as a chelate group. Further, the compound was claimed [1] as the first example of sexicovalent palladium(II). Repeated attempts by the present authors to prepare this compound always yielded Pd dpt_2 $dpth_2$ containing either 1 mol. of water or 0·5 mol. of methanol trapped in the lattice. This compound is monomeric in freezing benzene. Bivalent palladium is nearly always square-co-ordinated in its compounds and although some recent evidence of its possessing a distorted octahedral structure has been reported,[19] the latter configuration is not common. The compound Pd dpt_2 $dpth_2$ can be adequately formulated as containing square-co-ordinated palladium on the basis that both the ligand (dpth) and its anion (dpt) function as unidentate groups through one of the triazen nitrogen atoms (see XVI). Also the compounds Pd phen dpt_2, Pd py_2 dpt_2, and $PdCl_2$ $dpth_2$ can be similarly formulated as square-co-ordinated monomers. The dipyridine compound was monomeric in freezing benzene; the other compounds were not sufficiently soluble for molecular-weight measurements.



(XVI)



(XVII)



(XVIII)

In contrast to the corresponding diamagnetic palladium(II) compounds, the bivalent nickel compounds Ni dpt_2 py_2 and Ni dpt_2 phen are paramagnetic with magnetic moments (μ ~3·2 B.M./Ni) corresponding to two unpaired electrons. This excludes a square($3d4s4p^2$) arrangement and would suggest an octahedral $4s4p^34d^2$ one, although a tetrahedral configuration ($4s4p^3$) is also possible. Since these compounds are not sufficiently soluble for molecular-weight measurements it is probable that they possess polymeric octahedral structures based on the bridging arrangement (XIII) or (XIV)

The copper(I) and silver(I) compounds M dpt have been previously formulated [1] as bicovalent monomers involving the metal atom in bond angles of 90° (see I). However, all bicovalent copper(I) and silver(I) compounds examined structurally have been shown to be linear and, further, the four-membered ring arrangement indicated in (I) would lead to considerable steric strain. A dimeric structure as in (XVII) based on *syn–syn*-bonding XII) would permit linear co-ordination about the metal atoms.* Also, polymeric

* The postulated structure (XVII) has been recently verified for Cu dpt by Brown and Dunitz (Internat. Conference on Co-ordination Chemistry, London, April, 1959). The intramolecular Cu–Cu separation was reported as 2·6 Å.

[19] Harris and Nyholm, *J.*, 1956, 4375; Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127; Harris, Livingstone, and Reece, *Austral. J. Chem.*, 1957, **10**, 282; Harris, Livingstone, and Reece, *J.*, 1959, 1505.

structures based on (XIII) or (XIV) would enable the metal to be linearly co-ordinated. One such possible structure is (XVIII). It was not possible to differentiate between these structures by molecular-weight measurements since the copper(I) compound and the analogous silver compound were insufficiently soluble in boiling benzene.

Finally, it is interesting to contrast the slightly soluble mercury compound Hg dpt_2 with the dimeric Cu(II), Ni(II), and Pd(II) compounds. Mercury(II) in its quadricovalent complexes is tetrahedral, and such a bonding arrangement would not permit the mercury(II) compound to exist in the dimeric bridged form. However, a polymeric structure involving tetrahedral mercury is most likely. The dichloro-complex $HgCl_2$ 2dpth was also insufficiently soluble at the freezing point to permit molecular-weight measurements.

In conclusion, it appears that there is no substantial evidence that 1,3-diphenyltriazen can chelate to metals to give four-membered rings. In fact, the information adduced regarding the structures of the binuclear copper(II), nickel(II), and palladium(II) complexes strongly supports the *syn–syn*-bridging. The remaining bivalent palladium complexes can be adequately interpreted in terms of square rather than octahedral palladium(II) with the ligand or derived anion functioning as a unidentate group.

The authors are indebted to Dr. E. Challen for carrying out many microanalytical determinations for carbon, hydrogen, and nitrogen. One of them (B. F. H.) thanks the Australian Atomic Energy Commission for study leave.

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[*Received, March 6th,* 1959.]