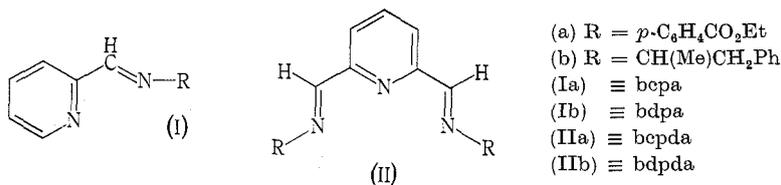


COPPER(II) COMPLEXES OF SOME PYRIDINE SCHIFF BASES*

By D. ST.C. BLACK†

Schiff bases (I) derived from pyridine-2-aldehyde and primary amines, are known¹⁻⁷ to function as bidentate ligands, while bis-Schiff bases (II) of pyridine-2,6-dialdehyde function as tridentates.^{4,5} Although these investigations have involved a variety of metal ions, they have usually concentrated on those metals which favour an octahedral configuration. Consequently, copper(II) complexes of these tridentate ligands have received little attention.



Lions and Martin⁵ have described a copper(II) complex of (II; R = -CH₂Ph) with two molecules of ligand to one copper atom, to which they have assigned an octahedral configuration.

This communication describes the copper(II) complexes formed with the tridentate ligands (IIa) and (IIb), together with those resulting from the related bidentate ligands (Ia) and (Ib) for comparison. This work arose in the context of a study of the biological properties of Schiff base-metal complexes derived from pyridine aldehydes and pharmacologically active amines.

Metal ions can facilitate⁸ Schiff base formation and it is usual¹⁻⁷ to prepare the Schiff base in the presence of the metal, and isolate the complex directly, rather

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¹ Busch, D. H., and Bailar, J. C., *J. Am. chem. Soc.*, 1956, **78**, 1137.

² Stratton, W. J., and Busch, D. H., *J. Am. chem. Soc.*, 1960, **82**, 4834.

³ Stoufer, R. C., and Busch, D. H., *J. Am. chem. Soc.*, 1956, **78**, 6016.

⁴ Figgins, P. E., and Busch, D. H., *J. Am. chem. Soc.*, 1960, **82**, 820.

⁵ Lions, F., and Martin, K. V., *J. Am. chem. Soc.*, 1957, **79**, 2733.

⁶ Krumholz, P., *Inorg. Chem.*, 1965, **4**, 609.

⁷ Burgess, J., and Prince, R. H., *J. chem. Soc. (A)*, 1967, 434; Burgess J., *J. chem. Soc. (A)*, 1967, 955.

⁸ Eichhorn, G. L., and Bailar, J. C., *J. Am. chem. Soc.*, 1953, **75**, 2905; Eichhorn, G. L., and Trachtenberg, I. M., *J. Am. chem. Soc.*, 1954, **76**, 5183.

than obtain it from a previously isolated ligand. Copper(II) complexes of ligands (IIa) and (IIb) were readily obtained by reaction of copper(II) chloride and pyridine-2,6-dialdehyde with ethyl *p*-aminobenzoate (benzocaine) and 1-phenyl-2-aminopropane (benzedrine) respectively. These complexes analysed for $\text{Cu}(\text{chel})\text{Cl}_2$ and conductance measurements showed both to be neutral. These data allow for two possible geometrical configurations, trigonal bipyramidal or square planar, depending on whether the ligand is respectively tridentate or bidentate. As ligands of type (II) are known to behave consistently as tridentates, it is reasonable to assign trigonal-bipyramidal configurations (Fig. 1) to these copper(II) complexes of (IIa) and (IIb).

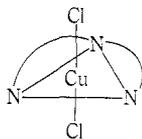
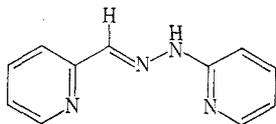


Fig. 1

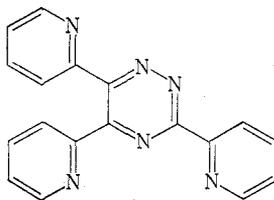
Since the ligand donor atoms are constrained to one plane, the ligand would be equatorially situated, with chlorine atoms above and below this equatorial plane.

Visible absorption maxima occur at $830\text{ m}\mu$ for orange $\text{Cu}(\text{bcpsa})\text{Cl}_2$ and $795\text{ m}\mu$ for green $\text{Cu}(\text{bdpsa})\text{Cl}_2$. Both complexes are paramagnetic.

Trigonal-bipyramidal complexes of copper(II) occur⁹ with a variety of ligands. The only tridentate chelate complex for which this configuration has been verified by X-ray crystallography is dichloroterpyridinecopper(II).¹⁰ Copper(II) complexes of two other tridentate ligands, pyridine-2-aldehyde-2'-pyridylhydrazone¹¹ (III) and 3,5,6-tri(2'-pyridyl)-1,2,4-triazine¹² (IV), have been considered to be trigonal bipyramidal, based only on analytical and conductance data. However, in all these examples, there exists an arrangement of donor atoms similar to that in terpyridine. It is possible that the phenomenon is quite general.



(III)



(IV)

Both 1 : 1 and 1 : 2 copper(II) complexes of ligands (Ia) and (IIa) can be prepared in the usual way. Only the 1 : 1 complex chlorides $\text{Cu}(\text{bcpsa})\text{Cl}_2$ and $\text{Cu}(\text{bdpsa})\text{Cl}_2$ are described here for comparison with $\text{Cu}(\text{bcpsa})\text{Cl}_2$ and $\text{Cu}(\text{bdpsa})\text{Cl}_2$. Both are green, with visible absorption maxima at $795\text{ m}\mu$ and $735\text{ m}\mu$ respectively. They are non-electrolytes and paramagnetic and are undoubtedly of square-planar configuration.

⁹ Muetterties, E. L., and Schunn, R. A., *Q. Rev. chem. Soc.*, 1966, **20**, 245.

¹⁰ Morgan, Sir Gilbert, and Burstall, F. H., *J. chem. Soc.*, 1937, 1649; Corbridge, D. E. C., and Cox, E. G., *J. chem. Soc.*, 1956, 594.

¹¹ Geldard, J. F., and Lions, F., *Inorg. Chem.*, 1965, **4**, 414.

¹² Geldard, J. F., *Inorg. Chem.*, 1965, **4**, 417.

Experimental

All infrared spectra were measured using a Perkin-Elmer IR 257 grating spectrometer and visible spectra using a Unicam SP 700 spectrophotometer.

Dichloro[2,6-pyridylene-bis(ethyl p-methyleneaminobenzoate)]copper(II)

Ethanollic solutions of benzocaine (0.33 g), pyridine-2,6-dialdehyde (0.14 g), and copper(II) chloride dihydrate (0.17 g) were mixed and heated for a few minutes on a water-bath. The resulting solution was allowed to cool and the compound precipitated as orange *crystals*, which were collected and recrystallized from dimethylformamide; yield 0.5 g (Found: C, 52.8; H, 4.2; Cu, 11.4; N, 7.6. $C_{25}H_{23}Cl_2CuN_3O_4$ requires C, 53.2; H, 4.1; Cu, 11.4; N, 7.4%).

The compound decomposed in water. It had a molar conductance of 0.017 ohm^{-1} in nitrobenzene, a magnetic moment of 1.98 B.M. at 21.5° , and it exhibited a visible absorption maximum at 830μ . It absorbed in the infrared at 1710, 1612, 1596, 1575, 1502, 1475, 1440, and 1418 cm^{-1} .

Dichloro[2,6-pyridylene-bis(1'-phenyl-2'-methyleneaminopropane)]copper(II)

Ethanollic solutions of benzedrine (0.27 g), pyridine-2,6-dialdehyde (0.14 g), and copper(II) chloride dihydrate (0.17 g) were mixed and heated for a few minutes on a water-bath. The resulting solution was allowed to cool and the compound precipitated as green *crystals*, which were collected and recrystallized from dimethylformamide; yield 0.5 g (Found: C, 59.5; H, 5.6; Cl, 14.3; Cu, 12.8; N, 8.1. $C_{25}H_{27}Cl_2CuN_3$ requires C, 59.5; H, 5.4; Cl, 14.1; Cu, 12.6; N, 8.3%).

The compound decomposed in boiling water. It had a molar conductance of 0.025 ohm^{-1} in nitrobenzene, a magnetic moment of 2.02 B.M. at 22° , and it exhibited a visible absorption maximum at 795μ . It absorbed in the infrared at 1602, 1586, 1564, 1496, 1478, and 1440 cm^{-1} .

Dichloro[ethyl p-(2-pyridylmethyleneamino)benzoate]copper(II)

Ethanollic solutions of benzocaine (0.17 g), pyridine-2-aldehyde (0.11 g), and copper(II) chloride dihydrate (0.17 g) were mixed and heated for a few minutes on a water-bath. The resulting solution was allowed to cool and the compound precipitated as green *crystals*, which were collected and washed with cold ethanol; yield 0.4 g (Found: C, 46.7; H, 3.9; Cl, 18.1; Cu, 15.7; N, 7.2. $C_{15}H_{14}Cl_2CuN_2O_2$ requires C, 46.4; H, 3.6; Cl, 18.2; Cu, 16.3; N, 7.2%).

The compound was insoluble in water. It had a molar conductance of 0.09 ohm^{-1} in nitrobenzene, a magnetic moment of 1.88 B.M. at 20.5° , and it exhibited a visible absorption maximum at 795μ . It absorbed in the infrared at 1708, 1630, 1602, 1596, 1574, 1500, 1480, 1450, and 1416 cm^{-1} .

Dichloro[1-phenyl-2-(2'-pyridylmethyleneamino)propane]copper(II)

Ethanollic solutions of benzedrine (0.14 g), pyridine-2-aldehyde (0.11 g), and copper(II) chloride dihydrate (0.17 g) were mixed and heated for a few minutes on a water-bath. The resulting solution was allowed to cool and the compound precipitated as fine, green *crystals*, which were collected and washed with cold ethanol; yield 0.35 g (Found: C, 50.0; H, 4.1; Cl, 20.2; Cu, 17.6; N, 7.4. $C_{15}H_{16}Cl_2CuN_2$ requires C, 50.2; H, 4.5; Cl, 19.8; Cu, 17.7; N, 7.8%).

The compound was insoluble in water. It had a molar conductance of 0.08 ohm^{-1} in nitrobenzene, a magnetic moment of 1.96 B.M. at 22° , and it exhibited a visible absorption maximum at 735μ . It absorbed in the infrared at 1648, 1602, 1575, 1496, 1480, and 1440 cm^{-1} .

Acknowledgment

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