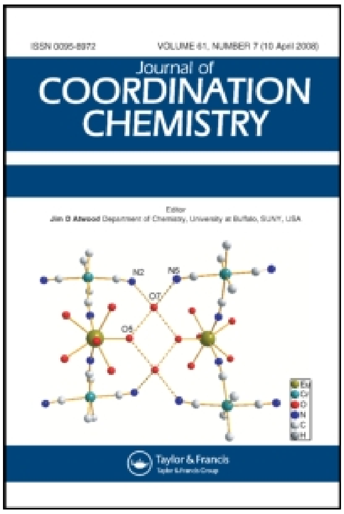

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Bis-(5-ethyl, 5-phenylbarbiturato)-bisimidazole Complexes of Copper(II), Nickel(II), and Cobalt(II)

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SHORT COMMUNICATION

Bis-(5-ethyl, 5-phenylbarbiturato)-bisimidazole Complexes of Copper(II), Nickel(II), and Cobalt(II)†

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In a recent communication Wang and Craven[1] reported that in the bis (5,5-diethylbarbiturato)-bisimidazole complexes of cobalt(II) and zinc(II), the metals are tetrahedrally coordinated by nitrogen atoms. These authors[2–3] have also shown that the corresponding nickel(II) complexes crystallize in three crystalline forms (green, orange, and pale-blue) and each form corresponds to a different arrangement of ligands around the central nickel atom (Table I). They have also shown by X-ray crystallography that the corresponding copper(II) and a pale-blue crystalline form of the nickel(II) complexes are six-coordinated as shown in Figure 1. Here, each metal is coordinated in a square-planar arrangement by a N

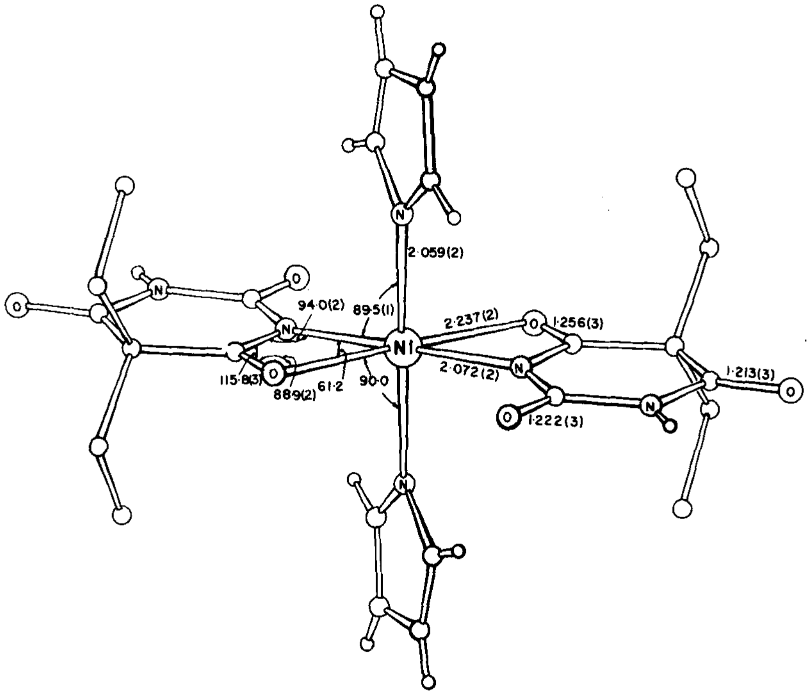

FIGURE 1 The molecular geometry of the pale-blue form of bis(5,5-diethylbarbiturato)-bisimidazole complex of nickel(II). The molecule has a center of symmetry at the nickel atom.

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and O from each barbiturate (5,5-diethylbarbiturate) residue forming unusual four-membered rings. Because of this interesting stereochemical finding, and because of the biological importance of barbiturate complexes, the corresponding phenobarbiturate (5-ethyl, 5-phenylbarbiturate) complexes have been prepared and investigated.

Each complex was prepared by adding a filtered aqueous solution of the metal chloride to an aqueous solution containing sodium phenobarbital and imidazole in the mole ratio of 1:2:2. The highly insoluble complexes were formed in quantitative yield and after filtering off, they were washed with water, then with ethanol and dried over P_2O_5. The copper(II) complex was fully analyzed.

Anal. Calcd. for $CuC_{30}H_{30}N_8O_6$: Cu, 9.6; C, 54.4; H, 4.6; N, 16.9. Found: Cu, 9.2; C, 54.2; H, 4.6; N, 16.7.

The other complexes were analyzed for metal only. Relevant data are recorded in Table II.

The infrared spectra of these complexes were recorded on KBr wafers with a Beckman IR-20 spectrophotometer. All show an intense band at ~540 cm^{-1} and another less intense band at ~500 cm^{-1} which may be assigned to the M–N stretching frequency.

Magnetic susceptibilities were measured on a Faraday balance at four different field strengths. The magnetic moment is calculated by the equation, $\mu_{eff} = 2.83\sqrt{\chi_m T}$, where χ_m is molar susceptibility, corrected for the diamagnetic contribution. The results are recorded in Table III. We have not used the equation, $\mu = 2.83\sqrt{\chi(T-\theta)}$, where θ is the Weiss constant, because Cotton and Wilkinson[4] have recommended that the best practice is to obtain a magnetic moment at a given temperature using the Curie law, and call this an effective magnetic moment, μ_{eff}, at the specified temperature.

X-ray diffraction powder patterns were measured with a GE SPG spectrogoniometer using Cu Kα radiation. The results are shown in Figure 2. The diffraction patterns indicate that the relative peak positions of $Ni(PB)_2(Im)_2$ are very similar to those of $Cu(PB)_2(Im)_2$, especially in the 2θ region of 8°–25°. This indicates that it is very likely that $Ni(PB)_2(Im)_2$ and $Cu(PB)_2(Im)_2$ are isomorphous and that the nickel and copper complexes have the same geometry. However, the powder diffraction patterns of the nickel and copper complexes seem to differ more than they should do if these complexes were perfectly isostructural. This may indicate that, while the gross structures of the nickel and copper complexes are similar, there are some finer structural differences.

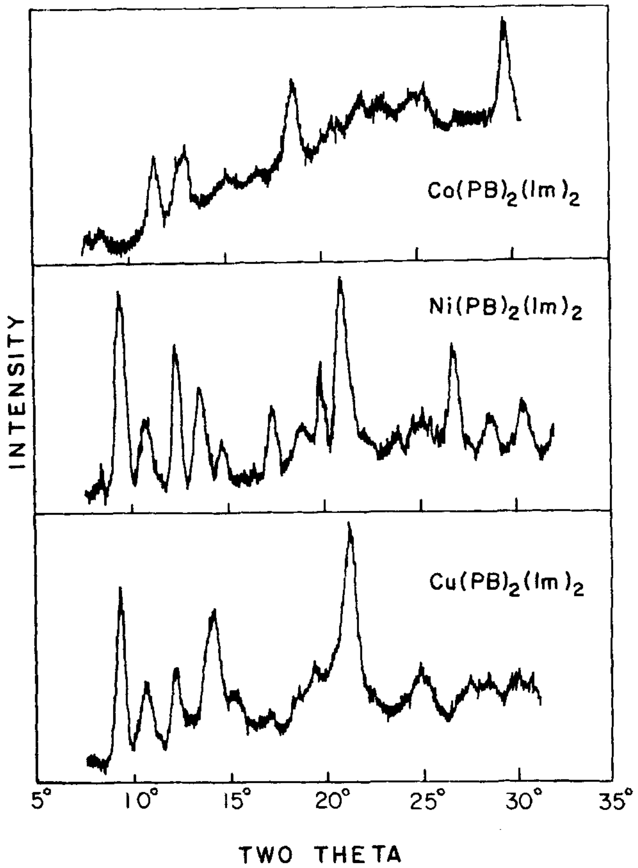
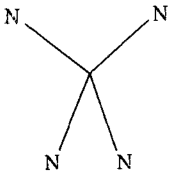
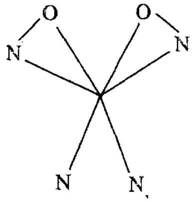
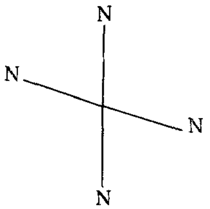
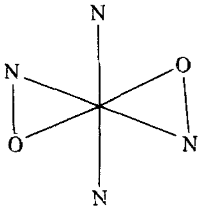
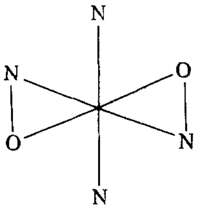
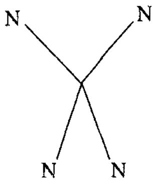
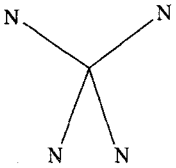
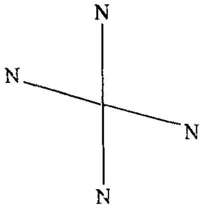
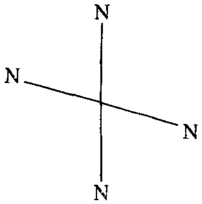


FIGURE 2 X-ray powder diffraction patterns of metal-phenobarbiturate-imidazole complexes.

As shown in Table III, the orange-coloured $Ni(PB)_2(Im)_2$ is diamagnetic. Therefore, it is reasonable to assume that the nickel atom is coordinated in a square-planar arrangement. Although the magnetic susceptibility measurement of $Cu(PB)_2(Im)_2$ complex does not give any conclusion as to the copper coordination, it does not rule out the possibility of a square-planar arrangement. Therefore, from the X-ray diffraction data described above, we conclude that the $Cu(PB)_2(Im)_2$ complex is also square-planar.

The above findings for the phenobarbiturate-imidazole complexes of nickel(II) and copper(II) are different from those of the corresponding barbiturate-imidazole complexes as shown in Table 1. These differences may be caused by the steric hindrance of the bulky phenyl group in phenobarbital. In Figure 1 the rather long Ni–O distance (2.237 A) in the pale-blue form of the barbiturate-imidazole complex

TABLE I
Coordination geometry of $M(B)_2(Im)_2$ and $M(PB)_2(Im)_2$ complexes

Central Atom	Co(II)	Ni(II)			Cu(II)	Zn(II)
Color of Complex	Purple	Green	Orange	Pale Blue	Pale Purple	Colorless
$M(B)_2(Im)_2$	Tetrahedral  	Distorted Octahedral?  	Square Planar  	Distorted Octahedral  	Distorted Octahedral  	Tetrahedral 
$M(PE)_2(Im)_2$	Tetrahedral  		Square Planar  		Square Planar  	

B = barbiturate, PB = phenobarbiturate, Im = imidazole indicates that the oxygen atom is not tightly bound to the nickel atom. This may explain the easy breakage of this bond, in forming the orange-colored, four-coordinated nickel(II) complex and the six-coordinated green complex, as indicated in Table I.

The magnetic moments of $Co(PB)_2(Im)_2$ and $Co(B)_2(Im)_2$ are 4.45 and 4.56 B.M., respectively. This corresponds to a high-spin tetrahedral configuration. According to Graddon, *et al.*,[5] such complexes have magnetic moments in the range of 4.1–4.7 B.M., which is close to the "spin-only" value of 3.89 B.M.

The experimental μ_{eff} is greater than the spin-only moment, because the orbital motion of the electrons also makes a contribution to the moment. The diffuse reflectance spectra of $Co(PB)_2(Im)_2$ and $Co(B)_2(Im)_2$ have been obtained by Dr. E. S. Hodge and are shown to be similar. Since the magnetic moment and reflectance spectra of $Co(PB)_2(Im)_2$ are similar to those of $Co(B)_2(Im)_2$, we suggest that the two cobalt complexes have the same configuration. In a previous paper,[1] Wang and Craven have carried out detailed X-ray crystal structure on $Co(B)_2(Im)_2$ and reported it to be tetrahedral. We conclude therefore that $Co(PB)_2(Im)_2$ is also tetrahedral.

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TABLE II
Data for $M(PB)_2(Im)_2$ complexes
PB = phenobarbiturate, Im = imidazole

Metal, M	Copper	Nickel	Cobalt
Color	pale-purple	light-orange	purple
M.P.	~280°	> 300°	~175°
Metal analysis			
Calcd:	9.6	8.9	8.96
Found:	9.2	8.9	8.6

TABLE III
Magnetic data for metal-barbiturate-imidazole complexes
PB = phenobarbiturate, B = barbiturate, Im = imidazole

Compound	Color	Electronic configuration of metal ion	μ_{eff} 23°	Geometry
$Co(PB)_2(Im)_2$	purple	d^7	4.45 B.M.	Tetrahedral
$Co(B)_2(Im)_2$	purple	d^7	4.56	Tetrahedral
$Ni(PB)_2(Im)_2$	orange	d^8	0	Square-planar
$Cu(PB)_2(Im)_2$	pale-purple	d^9	1.75	Square-planar