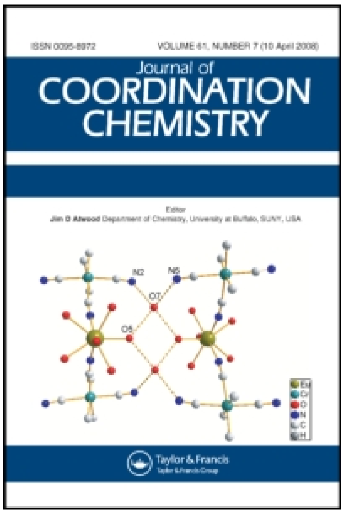

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BINUCLEAR METAL CHELATES OF BISACETYLACETONE BIPHENYLDIHYDRAZONE

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BINUCLEAR METAL CHELATES OF BISACETYLACETONE BIPHENYLDIHYDRAZONE

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Reaction of bihenyl-4,4′-tetrazonium ion with 2,4-pentanedione leads to 3,3′-(4,4′-biphenyldihydrazoni)bis-(2,4-pentanedione). The compound exists in the intramolecularly hydrogen bonded dihydrazone state. Copper(II), nickel(II) and palladium(II) complexes having the composition M_2L_2 have been synthesised and characterised. Ir, ^1H and ^{13}C nmr and mass spectroscopic data clearly indicate the binucleating nature of the chelates in which the hydrogen bonded carbonyls and one of the hydrazono nitrogens of each pentanedione group are involved in bonding with the metal ion.

KEY WORDS: Hydrazones, binuclear ligands, synthesis, complexes.

INTRODUCTION

Polydentate chelating ligands with isolated donor sets separated by aromatic or other bridging functions capable of simultaneously binding two metal ions have considerable importance as model compounds for certain metallobiomolecules.[1] Schiff base condensation is one of the most widely employed methods for the synthesis of such binucleating ligands. The reactivity of 1,3-diketones and their metal derivatives has led to the design and synthesis of a large number of such polydentate and macrocyclic ligand systems.[1,2] Our interest[3] in the synthesis of polydentate and macrocyclic chelates by the reaction of arene diazonium and tetrazonium ions with 1,3-diketones and metal 1,3-diketonates led us to the synthesis and characterisation of the binucleating ligand 3,3′-(4,4′-biphenyldihydrazono)bis(2,4-pentanedione), (bisacetylacetone-biphenyldihydrazone, H_2L) and its copper(II), nickel(II) and palladium(II) chelates.

EXPERIMENTAL

The ligand was prepared by coupling tetrazotized benzidine with 2,4-pentanedione. Benzidine was tetrazotized as reported[4] using $NaNO_2$ and HCl. The tetrazonium chloride solution (0.01 mol) was slowly added with stirring to a solution of acetylacetone (0.02 mol in 25 cm^3 methanol). Sodium acetate was added to maintain the pH of the mixture between 6–7. Stirring was continued for about 1 h. The precipitated product was filtered, washed with water and recrystallised from hot benzene.

Table 1 Physical and analytical data for the compounds

		Found %				Calculated %			
Compound	M.P. (°C)	M	C	H	N	M	C	H	N
H_2L	225		64.85	5.23	13.36		65.63	5.42	13.79
Cu_2L_2	231	13.16	55.98	4.01	11.31	13.58	56.57	4.27	11.97
Ni_2L_2	290	12.28	56.55	4.12	11.86	12.72	57.63	4.32	12.72
Pd_2L_2	240		51.10	3.58	10.40		51.72	3.91	10.97

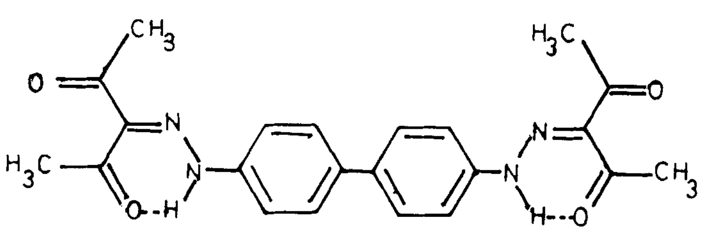
For preparing metal complexes a concentrated aqueous solution of metal salt (0.001 mol, acetates of Cu^{2+} and Ni^{2+} and chloride of Pd^{2+}) was added to a solution of the ligand (0.001 mol) in methanol, refluxed for 2 h and cooled to room temperature. The precipitated complex was filtered and washed with water, recrystallised from hot ethanol and dried in vacuum. Analytical data are given in Table 1.

Infrared spectra (KBr pellets) were recorded on a Pye-Unicam SP 2000 spectrometer and NMR spectra on a Varian XL-100 FT spectrometer ($CDCl_3$/TMS solutions). Mass spectra were recorded on a JEOL SX-102 mass spectrometer (FAB using argon). Thermograms were obtained using a Stanton thermal balance.

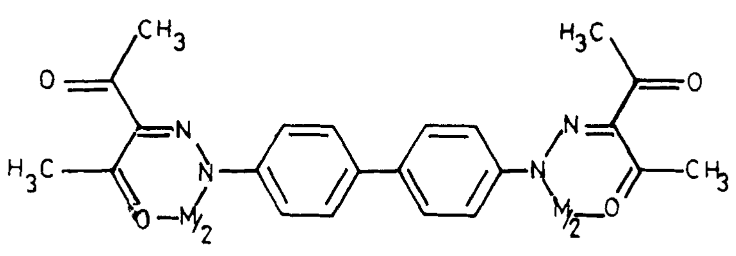
RESULTS AND DISCUSSION

Favrel,[5] as early as 1899, reported the formation of dihydrazones by the reaction of tetrazotized benzidine with 1,3-diketones. However, reports are scanty on structural aspects of these compounds. Therefore, it was necessary to characterise the ligand. Ir, ^1H and ^{13}C nmr data of the compound are consistent with the structure Ia.

Thus, the ir spectrum of the compound in the region 1600–1800 cm^{-1} showed two strong bands at 1680 and 1620 cm^{-1}, assignable respectively to stretching of free and hydrogen bonded acetyl carbonyl groups.[3,6,7] The spectrum displayed a very broad band in the region 3375-2400 cm^{-1} for the chealted NH function. In accord with the internally hydrogen bonded structure, the ^1H nmr spectrum showed two methyl proton signals of equal intensity (Table 3). Absence of methine proton signals and the presence of a low field, two proton signal[7] at 15.45 δ for the chelated hydrazone proton agrees well with the structure Ia. That the compound contains two types of methyl groups and carbonyls is evident from the observed ^{13}C nmr data (Table 3).



Ia



Ib M = Cu(II), Ni(II), Pd(II)·

The mass spectrum of the compound is dominated by an intense $(M+1)^+$ peak at *m/e* 407. The spectrum shows that the fragmentation pattern differs considerably from reported spectra of 2,4-pentanediones. For example, ketene elimination, (M-42), characteristic of acetylacetone, is absent. Cleavage in the case of hydrazones usually occurs at the N-N bond, and, in the case of azo compounds, on both sides of the azo group.[8,9] If cleavage of the compound under consideration occurred on ether side of the N-N linkage, the resulting ion would have undergone a similar fragmentation as with acetylacetone. The appearance of a peak at *m/e* 295 (M-$C_511_5O_2N$) indicates that cleavage occurs first at one of the N-N bonds; this is followed by the scission of the second N-N bond (fragments of *m/e* 183–185). Prominent peaks found in the spectrum are given in Table 4.

All the metal complexes behaves as non-electrolytes (sp. cond. $<10\Omega^{-1}$ cm^{-1} mol^{-1} in methanol) and do not contain the anion of the metal salt used for their preparation. The copper(II) complex has a magnetic moment of 1.78 BM. Nickel(II) and palladium(II) cmplexes are diamagnetic. The compositions of the complexes on the basis of elemental analyses are given in Table 1.

Ir spectra of the complexes are compatible with the structure that would result if the chelated hydrogens are replaced by metal ions, as in structure Ib. Thus the position of the free carbonyl band of the ligand is only margianlly altered in the spectra of the chelates. The band at 1640 cm^{-1} due to the hydrogen bonded acetyl carbonyl group disappeared in the spectra of the complexes. Instead, a new band appeared at ~1570 cm^{-1} in the spectra of all complexes (Table 2). This band can be assigned to the stretch of the metal bonded carbonyl group.[3,10] A weak band attributable to conjugated ν C=N appears at ~1615 cm^{-1} in the spectra of all complexes. In the

Table 2 Principal ir frequencies (cm^{-1}) for the compounds

Compound	ν C=O Free	 Chelated	ν C=N ν C=C	νM-N	νM-O
H_2L	1680s	1630s	1595m		
Cu_2L_2	1675s	1572s	1615m 1600m	545	428
Ni_2L_2	1678s	1570s	1617m 1598m	538	425
Pd_2L_2	1675s	1568s	1618m 1590m	535	420

Table 3 NMR data (ppm) for the compounds

Compound	^1H nmr chemical shift[a]		^{13}C nmr chemical shift			
	Methyl	Aryl	Methyl	Aryl	C=N	Carbonyl
H_2L	2.55 (6H,s)	7.50–7-70 (8H,m)	31.65	137.10, 128.40	142.48	195.10
	2.62 (6H,s)		26.64	127.28, 116.50		196.12
Ni_2L_2	2.50 (12H,s)	7.30–7.80 (16H,m)	31.61	136.58, 127.88	141.59	195.65
	2.65 (12H,s)		26.81	127.36, 117.30		197.11
Pd_2L_2	2.51 (12H,s)	7.30–7.80 (16H,m)	31.64	137.10, 128.08	141.20	195.80
	2.70 (12H,s)		26.32	127.90, 116.80		198.10

[a] S = singlet, m = multiplet.

Table 4 Important *m/e* peaks in the mass spectra of the compounds

Compound[a]	*m/e*
H_2L	408, 407, 406, 295, 296, 185–182, 149, 150, 138, 120, 107, 95, 91–89, 77, 69, 55, 43, 41.
Cu_2L_2	938, 934, 830, 807, 741, 655, 629, 528-532, 468, 470, 424, 342, 344.
Ni_2L_2	926–924, 880–883, 866, 820, 760, 671, 636, 611, 561, 522–520, 460–463, 431.
Pd_2L_2	1020–1022, 786, 706, 612–614, 982, 510–512, 440.

[a] In the case of metal chelates, only prominent, metal containing ions having a relative intensity > 1% are given.

spectrum of the ligand, this band is presumably masked by the strong absorption of the hydrogen bonded carbonyl group occurring in the same region. The broad free ligand band in the region 3400-2400 cm^{-1} cleared up in the spectra of the metal chelates and instead weak bands around 3050 cm^{-1} (aromatic ν C-H) and in the region 2950-2850 cm^{-1} (ν C-H of methyl groups) appeared in the spectra of all chelates. Two medium intensity bands not found in the spectrum of the ligand at about 540 and 425 cm^{-1}, but observed in the spectra of chelates, can be assigned to ν M-N and ν M-O, respectively.[3,11]

In conformity with the structure proposed, the ^{1}H nmr spectra of the nickel(II) and palladium(II) chaltes show two methyl proton signals of equal intensity. The low field signal at 15.45 δ due to the chelated hydrogens of the free ligand disappeared in the spectra of the chelates. The integrated intensities of aryl protons and methyl proton signals and the ^{13}C nmr data (Table 3) agree well with the binucleating nature of the chelates.

All chelates show a molecular ion peak (*m/e* corresponds to the composition M_2L_2). Peaks due to the fragments (M_2L_2-CH_3CO), (M_2L_2-$2CH_3CO$), M_2L and ML are comparatively more intense than the molecular ion peak. The most intense peak in the spectra of all chelates corresponds to the free ligand (*m/e* 407). The fragmentation pattern below *m/e* 407 in the spectra of all chelates is more or less similar to that of the free ligand, except that, in the former, several metal containing fragments can be located (Table 4).

Thermograms of all chelates (in air) do not show any weight loss until 200°C, indicating the absence of any water of hydration.

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