March, 1980] © *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***53***, *809—810 (1980)* 809

Syntheses and Electronic Spectra of 4,4′-Diacetyl-2,2′-isopropylidenedi-8-quinolinol, Its Nickel(II), Copper(II), and Zinc(II) Chelates

Yoshinori YAMAMOTO,* Kunio SHIBAHARA, and Shinsuke TAKEI

Department of Industrial Chemistry, Faculty of Engineering,
Ibaraki University, Nakanarusawa-cho, Hitachi 316

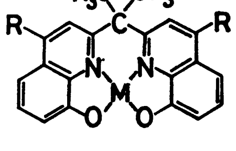
(Received July 2, 1979)

Synopsis. The title nickel chelate, which has a planar four-coordinated form, gave an intense new band, no corresponding band of which was observed with the other chelates, at the position between the first and second π-π^* bands. The spectra were compared with those of the corresponding compounds free from the acetyl group.

The crystalline compounds, Ni-, Cu-, and Zn(aipdq), have been obtained readily by the reaction of each of the metal ions with the ligand. The absorption data are given in Tables 1 and 2. The intra-ligand transition bands, termed the A-, B-, and C-bands, of each of the M(aipdq) can well be compared with those[1] of the corresponding chelates free from the acetyl group, M(ipdq), in the same solvents. Both Cu- and Zn(aipdq) in all the solvents and Ni(aipdq) in pyridine give similar spectral shapes (Table 1). When the solvents listed in Table 2 are used, the spectral shapes of the A- and C-bands of Ni(aipdq) are remarkably changed, together and an intense new band appears. A similar behavior was observed with the M(ipdq). The new band of Ni(aipdq) can be compared with an unassigned small shoulder band observed with planar four-coordinated Ni(ipdq).

On the basis of the d-d spectrum, Ni(aipdq) in pyridine is found to be coordinated by two pyridine molecules (Table 1). Both in the solid state and in *N*,*N*-dimethylformamide (DMF) (8×10^{-3} M, 1 cm cell), Ni(aipdq) gives no peak near 10000 cm^{-1}, suggesting[2] that the compound has a planar four-coordinated form (*cf.* Table 2). With the other solvents for Ni(aipdq), the measurement could not be performed because of their low solubilities, but a planar form can be expected because these solutions give intense bands similar to those in DMF (Table 2).

For the spectra of the planar nickel chelates, it is observed that, upon acetylation, both the C-band and the new band shift to the red, 1.3—1.6 and *ca.* 2×10^3 cm^{-1} respectively, in the same solvents. The C-bands of the M(ipdq) have been described in terms of the movement of the electronic charge from the phenol ring to the pyridine ring.[1] The decrease in the electron density in the pyridine ring upon the acetylation explains the movement of the C-bands to lower energies, though it should be noted that the quantity of the shift of the planar nickel chelate is less than those (2.2—2.4×10^3 cm^{-1}) of the other chelates. The new band of planar Ni(aipdq) is not a part of the B- or C-band, since, when the solvent is changed to MeOH, the new band shifts strongly to the blue, despite the small shift of the B-band, while upon changing to the solid state the new band shows only a little change, despite a complex splitting of the C-band (Table 2). These observations suggest that the new band is to be described in terms of the charge transfer from metal to the ligand (MLCT). In the other chelates, the lack of the corresponding band near the B- or C-band is in contrast with the well-known MLCT of the Cu(II), Ni(II), *etc.* complexes with pyridine *N*-oxide and its derivatives, whose positions change slightly when the central metal is changed.[3] From the viewpoint of the development of *selective* colorimetric reagents for nickel analysis, it would be interesting to search for a modification of the ligand which would cause such a new band to appear in a lower energy range than the first π-π^* bands of the chelates.



M(aipdq), R=COCH_3
M(ipdq), R=H
M=Ni(II), Cu(II),
or Zn(II)

Experimental

The measurement and analyses were made by the same methods as in the previous paper.[1] Zn(ipdq) was prepared in a way similar to that[1] used for of Cu(ipdq); it was dried at 120 °C to give a deep yellow, crystalline powder. Found: Zn, 16.48%. Calcd: 16.60%.

4,4′-Diacetyl-2,2′-isopropylidenedi-8-quinolinol: This was prepared by a method similar to that developed by an Italian group.[4] To a solution of Ni(ipdq) (or ipdq) (10 mmol) in 40 cm^3 of EtOH and 8 cm^3 of concd H_2SO_4, $AgNO_3$ (0.4 g) in 80 cm^3 of water was added; the mixture was then heated at 40—50 °C and stirred for 2 h. During heating, pyruvic acid (8 cm^3) and $(NH_4)_2S_2O_8$ (10 g in 80 cm^3 of water) were added in two equal portions at hourly intervals. After cooling, the precipitate was collected, treated with 60 vol% aq EtOH (150 cm^3) containing AcOK (3.6 g), recollected, washed with water, and dried to give the crude product. Repeated recrystallization from toluene (45 cm^3 per 1.0 g), using activated characoal, gave yellow needles (1.3 g, 31%): mp 200.5—201.5 °C. Found: C, 72.17%; H, 5.20%. Calcd for $C_{25}H_{22}N_2O_4$: C, 72.45%; H, 5.35%. PMR ($CDCl_3$): δ=2.06 (6H, s, $>C(CH_3)_2$), 2.59 (6H, s, $-COCH_3$), 7.15—7.90 (8.8H, m, ring proton and a part of OH). IR (KBr): 3415 (OH), 1699, and 1678 cm^{-1} (C=O). UV$_{\text{max}}$: (Cyclohexane) 37.17×10^3 cm^{-1} (log ε 4.68) (A-band), 30.35 (3.67) and 29.33 (3.69) (B-band), 27.0 (sh 3.46) (C-band); (MeOH) 37.59 (4.67), 30.8 (sh 3.75) and 29.85 (3.76), 27.4 (sh 3.50); (0.1 M aq NaOH) 35.27 (4.59), 30.3 (sh 3.66) and 29.2 (sh 3.61), 25.2 (3.55); (6.0 M aq HCl) 36.36 (4.70), 30.8 (sh 3.86) and 29.67 (3.94), 25.3 (3.40).

(4,4′-Diacetyl-2,2′-isopropylidenedi-8-quinolinolato)nickel(II), Ni(aipdq): To a warmed solution of $Ni(OAc)_2\cdot4H_2O$ (1 mmol in 30 cm^3 of EtOH), a hot solution of the ligand (1 mmol in 20 cm^3 of acetone) was added. From the mixture shiny needles immediately separated out; they gradually

Table 1. The absorption data[a] of the metal chelates

Chelate	Solvent	A-band	B-band		C-band
		σ_{max}(log ε)	σ_{max}(log ε)	σ_{max}(log ε)	σ_{max}(log ε)
Zn(ipdq)	MeOH	38.54(4.75)	31.10(3.31)	29.50(3.30)	25.6(3.51)
	DMF		30.3 (sh 3.46)	29.11(3.52)	24.5(3.52)
	Pyridine		30.0 (sh 3.51)	28.92(3.58)	24.1(3.52)
Zn(aipdq)	MeOH	36.83(4.58)	30.5 (sh 3.38)	29.4 (sh 3.28)	23.3(3.39)
	DMF	35.84(4.50)	30.0 (sh 3.46)	28.9 (sh 3.39)	22.1(3.39)
	Pyridine		29.9 (sh 3.51)	28.8 (sh 3.46)	21.8(3.39)
Cu(aipdq)	MeOH	37.11(4.60)	30.70(3.35)	29.6 (sh 3.32)	23.2(3.46)
	DMF	36.30(4.59)	29.79(3.43)	28.9 (sh 3.39)	21.8(3.46)
	DCE[b]	36.32(4.59)	30.08(3.37)	29.0 (sh 3.31)	21.7(3.45)
	Pyridine		29.37(3.52)	28.5 (sh 3.50)	21.2(3.48)
	$CHCl_3$[c]	36.17(4.63)	29.99(3.41)	28.9 (sh 3.34)	21.5(3.49)
Ni(aipdq)	Pyridine[d]		29.0 (sh 3.64)	27.93(3.70)	21.2(3.44)

a) The wave numbers are given in 10^3 cm^{-1} units, and sh means a shoulder band. b) 1,2-Dichloroethane. c) Containing 0.5 vol% EtOH. d) The d-d bands: 12.7(sh 1.40) and 11.4(1.49).

Table 2. The absorption data[a,d] of Ni(aipdq)

Solvent	A-band		B-band		New band	C-band
	σ_{max}(log ε)	σ_{max}(log ε)	σ_{max}(log ε)	σ_{max}(log ε)	σ_{max}(log ε)	σ_{max}(log ε)
MeOH	42.64(4.56)	35.84(4.45)	29.9 (sh 3.58)	28.78(3.60)	27.2(sh 3.59)	22.3(3.67)
DMF[e]		34.60(4.36)	29.46(3.56)	28.6 (sh 3.55)	26.1(3.60)	21.1(3.68)
DCE[b]	41.41(4.63)	34.60(4.40)	29.28(3.58)	28.4 (sh 3.56)	25.8(3.61)	20.7(3.68)
$CHCl_3$[c]	41.41(4.61)	34.48(4.41)	29.28(3.58)	28.4 (sh 3.57)	25.8(3.60)	20.5(3.67)
solid[e,f]				28.8 (sh)	24.6	19.9[g]

a)—c) The footnotes are the same as those given in Table 1. d) The data of the pyridine solution are given in Table 1. e) The d-d band: 12.1 (ε: *ca.* 1) in DMF; 12.3 (weak sh) in the solid state, possibly a spin-forbidden band of a planar nickel chelate (Ref. 2). f) A mull method. A KBr disk technique gave a similar result. g) A very broad band accompanied by intense shoulder bands at 21.2, 18.1, and 16.9.

changed to plates. After cooling, the black-purple plates was collected, washed with EtOH, dried at 110 °C (a 94.5% yield), and recrystallized from DMF (20 cm^3 per 100 mg) by adding acetone (60 cm^3). Found: C, 63.82%; H, 4.44%; Ni, 12.47%. Calcd for $C_{25}H_{20}N_2O_4Ni$: C, 63.73%; H, 4.28%; Ni, 12.46%. IR (KBr): 1673 cm^{-1} (C=O).

Cu- and Zn(aipdq): These were prepared in ways similar to that used for of Ni(aipdq), using $Cu(OAc)_2 \cdot H_2O$ or $Zn(OAc)_2 \cdot 2H_2O$. The black needles of Cu(aipdq) were obtained in a 90.0% yield and were recrystallized from MeOH (120 cm^3 per 100 mg). Found: C, 63.19%; H, 4.47%; Cu, 13.37%. Calcd: C, 63.08%; H, 4.24%; Cu, 13.35%. IR (KBr): 1679 cm^{-1} (C=O). Zn(aipdq) (a 84.8% yield) was recrystallized from MeOH (80 cm^3 per 100 mg) to give deep maroon needles. Found: Zn, 13.40%. Calcd: Zn, 13.68%. IR: 1691 cm^{-1}.

The authors wish to thank Dr. Masahiko Takahashi for the elemental analyses.

References

1) Y. Yamamoto, A. Miura, A. Kawamata, M. Miura, and S. Takei, *Bull. Chem. Soc. Jpn.*, **51**, 3489 (1978).

2) M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, **9**, 311 (1972—1973), and the references cited therein.

3) W. Byers, B. Fa-Chun Chou, A. B. P. Lever, and R. V. Parish, *J. Am. Chem. Soc.*, **91**, 1329 (1969); N. M. Karayannis, A. N. Speca, D. E. Chasan, and L. L. Pytlewski, *Coord. Chem. Rev.*, **20**, 37 (1976), and the references cited therein.

4) T. Caronna, G. Fronza, F. Minisci, and O. Porta, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 2035.