Investigation into Aroylhydrazones as Chelating Agents. Part 4.[1] Synthesis and Spectroscopic Characterization of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} Complexes of 2,6-Diacetylpyridine Bis(2-thenoylhydrazone) and *X*-Ray Crystal Structure of Bis[2,6-diacetylpyridine bis(2-thenoylhydrazonato)(2−)]dizinc(II) †

Carlo Lorenzini, Corrado Pelizzi, Giancarlo Pelizzi,* and Giovanni Predieri
Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

Some new complexes of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with 2,6-diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) have been synthesized and examined by i.r. spectroscopy. The structure of $Zn_2(dapt)_2$ has been established by *X*-ray diffraction. Crystals are monoclinic, space group *C*2/*c*, with unit-cell dimensions a = 20.780(3), b = 17.162(2), c = 15.173(1) Å, β = 48.85(1)°, and Z = 4. The structure has been solved by the heavy-atom method and refined by full-matrix least-squares calculations to R = 0.0587 for 2 119 diffractometer data. The compound is dimeric with the pyridine ring unusually bridging two zinc atoms, which have a highly distorted octahedral co-ordination. The deprotonated ligand is not planar, the hydrazone side chains being considerably twisted out of the plane of the pyridine ring.

Our interest in the co-ordination chemistry of acylhydrazones has led to the synthesis and the structural characterization of a number of metal complexes of 2,6-diacetylpyridine aroylhydrazones (aroyl = benzoyl, picolinoyl, and salicyloyl).[1–4] Some interesting aspects involving the hydrazones have come from these investigations, for example the versatility in the co-ordination, the tendency to yield seven-co-ordinate stereochemistries, the ability to behave as neutral or deprotonated ligands, and the flexibility in assuming different conformations.

In an extension of these studies, which are carried out in order to obtain a fuller understanding of the influence exerted by the organic substituents and by the metal on the chemical and structural properties of the compounds, we have investigated the syntheses and structures of metal complexes of hydrazones having a different aroyl group, such as 2-thenoyl and 2-aminobenzoyl.

This paper reports the synthesis and the i.r. spectra of complexes obtained by reaction of 2,6-diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) with chlorides and acetates of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, and the crystal and molecular structure of $Zn_2(dapt)_2$.

Experimental

Materials.—2,6-Diacetylpyridine and 2-thiophenecarboxylic acid hydrazide were commercially available (Aldrich) and used without further purification.

Preparations.—2,6-Diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) was prepared by refluxing an ethanol solution of 2-thiophenecarboxylic acid hydrazide and 2,6-diacetylpyridine (2 : 1 molar ratio) for about 2 h. On cooling and standing overnight a pale yellow powder separated, which melts at 222 °C. The product was identified by C, H, and N analyses, by i.r. and mass spectra [m/e = 431 (21.9), 310 (18.8), 121 (100.0), 162 (78.1), 65 (79.7), and 93 (31.3%)].

Cobalt(II), nickel(II), copper(II), and zinc(II) complexes were prepared by treating a hot chloroform solution of H_2dapt with the metal chloride (or acetate), dissolved in warm methanol, in 1 : 1 molar ratio. The mixture was refluxed for about 1 h and then allowed to cool. When acetate was used, the complex precipitated more quickly than the corresponding chloride complex. From the reaction with $CuCl_2 \cdot 2H_2O$ a brown unidentified product was isolated.

Analytical data, which agree with the formulae $M(H_2dapt)Cl_2 \cdot 4H_2O$ (M = Co, Ni, or Zn) and $M(dapt) \cdot nH_2O$ (M = Ni, Cu, or Zn, n = 0; M = Co, n = 2), are available as Supplementary Material.

Measurements.—Elemental C, H, and N analyses were carried out on Perkin-Elmer model 240 automatic equipment. Metal analyses were done by atomic absorption spectroscopy on a Perkin-Elmer model 303 instrument. I.r. spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer. Mass spectra were determined with a Varian CH-5 spectrometer [70 eV (*ca.* 1.12 × 10^{-17} J)].

Crystal Structure Determination of $Zn_2(dapt)_2$.—Preliminary Weissenberg photographs showed monoclinic symmetry, the systematic absences for hkl reflections with $h + k = 2n + 1$ and for $h0l$ reflections with $l = 2n + 1$ led to *C*2/*c* or *Cc* as possible space groups. The former was chosen for structure determination on the basis of the distribution of normalized structure factors E and it was found to be correct. Unit-cell dimensions and their standard deviations were derived by least-squares analysis of the θ values of 23 computer-centred reflections.

Crystal data. $C_{38}H_{30}N_{10}O_4S_4Zn_2$, M = 949.72, Monoclinic, a = 20.780(3), b = 17.162(2), c = 15.173(1) Å, β = 48.85(1)°, U = 4 074(1) Å^3, D_m = 1.54, Z = 4, D_c = 1.548 g cm^{-3}, $F(000)$ = 1 936, μ(Cu-K_α) = 38.0 cm^{-1}.

Intensities were collected with a computer controlled Siemens three-circle diffractometer at room temperature using Ni-filtered Cu radiation (λ = 1.541 78 Å) in the conventional moving-crystal moving-counter scan mode, the drive speed being related to the number of counts on the peak (lowest speed 2.5° min^{-1}). A unique data set was measured in the scan range 2θ = 6.0—126.0° in the quadrant defined by $\pm h + k + l$, yielding 2 831 independent reflections; of

---

† *Supplementary data available* (No. SUP 23642, 19 pp.): thermal parameters, observed and calculated structure factors, full bond length and angle data, analytical data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Fractional atomic co-ordinates ($\times 10^4$)

Atom	X/a	Y/b	Z/c
Zn	4 121(1)	1 376(0)	4 032(1)
S(2)	2 791(1)	−1 501(1)	4 507(2)
O(1)	5 956(3)	1 955(2)	−249(4)
O(2)	3 068(3)	744(3)	4 678(4)
N(1)	5 914(4)	3 043(3)	709(5)
N(2)	5 982(3)	2 475(3)	1 309(5)
N(3)	5 740(3)	1 400(3)	2 800(5)
N(4)	4 554(3)	282(3)	3 848(5)
N(5)	3 986(4)	−301(3)	4 117(5)
C(5)	5 903(4)	2 689(4)	−49(6)
C(6)	6 133(4)	2 696(4)	1 972(6)
C(7)	6 242(6)	3 528(4)	2 152(7)
C(8)	6 222(4)	2 039(4)	2 533(6)
C(9)	6 800(5)	2 063(5)	2 690(7)
C(10)	6 931(5)	1 395(5)	3 064(8)
C(11)	6 468(5)	737(5)	3 312(7)
C(12)	5 858(4)	762(4)	3 199(6)
C(13)	5 275(4)	95(4)	3 532(6)
C(14)	5 532(5)	−729(4)	3 493(7)
C(15)	3 261(4)	18(4)	4 485(5)
C(16)	2 645(5)	−516(4)	4 652(6)
C(17)	1 913(5)	−304(4)	4 838(7)
C(18)	1 520(6)	−961(6)	4 804(9)
C(19)	1 923(7)	−1 646(5)	4 653(8)
S(1A)	5 795(4)	4 169(4)	−606(6)
S(1B)	5 886(6)	2 740(6)	−1 711(9)
C(1)	5 839(4)	3 201(4)	−766(6)
C(2A)	5 886(9)	2 985(9)	−1 678(14)
C(2B)	5 795(14)	4 052(13)	−837(20)
C(3)	5 855(6)	3 653(5)	−2 279(8)
C(4)	5 805(6)	4 299(5)	−1 736(8)
H(71)	5 638(66)	3 800(56)	2 471(92)
H(72)	6 806(68)	3 709(56)	1 411(95)
H(73)	6 159(60)	3 614(53)	2 961(91)
H(9)	7 161(46)	2 472(40)	2 447(65)
H(10)	7 413(55)	1 396(45)	3 144(76)
H(11)	6 515(48)	244(47)	3 577(73)
H(141)	6 152(55)	−758(47)	3 107(74)
H(142)	5 331(63)	−906(55)	4 175(88)
H(143)	5 349(57)	−1 111(54)	3 071(84)
H(17)	1 800(54)	118(42)	4 850(77)
H(18)	996(48)	−924(43)	4 986(66)
H(19)	1 729(46)	−2 095(43)	4 584(64)

these, 2 119 were deemed observed according to the criterion $I > 2\sigma(I)$ and were retained for refinement. Measurement of a standard reflection showed no deterioration during the time required to collect the data. These were reduced to structure amplitudes in the normal manner without correction for absorption because of the small crystal size.

Structure solution and refinement. The structure was solved by the heavy-atom technique. The Patterson function was utilized to determine the position of the zinc atom, while all the other non-hydrogen atoms were located from subsequent electron-density difference syntheses. The initial full-matrix least-squares isotropic refinement, which converged at $R = 0.1265$ indicated that one of the two thiophene rings exhibited disorder at the S(1) and C(2) positions, as U for S(1) was *ca.* 1.5 times the value for S(2), while the value of U for C(2) was unreasonably low. In addition, a difference-Fourier map showed a peak of height 2.0 e Å^{-3}, 0.45 Å from C(2). On the basis of peak weights of a subsequent ΔF map, computed leaving out both these atoms, the two positions were assigned occupancy factors of 0.60 [S(2A) and C(2A)] and 0.40 [S(2B) and C(2B)]. Continued least-squares refinement of the atomic co-ordinates and anisotropic thermal parameters for all non-hydrogen atoms other than those belonging to the disordered thiophene ring, which were refined isotropically, resulted in a R value of 0.0940. Twelve of the 15 hydrogen atoms were located on a ΔF map and their contributions were included in subsequent structure factor calculations. The three hydrogens of the disordered thiophene could not be located. In the final cycles of least-squares refinement 293 parameters were refined; a scale factor, co-ordinates of 43 atoms, anisotropic thermal parameters for 24 atoms, and isotropic thermal parameters for 19 atoms. The function minimized was $\Sigma w|\Delta F^2|$, the weight w being unity at first, while in the final stage of refinement the weighting scheme $w = 1/\sigma^2(F_o) + 0.005\ F_o^2$, derived from counting statistics, was introduced. Final discrepancy factors were $R = 0.0587$ and $R' = 0.0748$. A difference-Fourier synthesis at the end of the refinement showed no undesirable features. Scattering factors used in the structure factor calculations were taken from ref. 5, and allowance was made for anomalous dispersion. Computations were carried out using the SHELX 76 system of programs [6] on the Cyber 76 computer of Centro di calcolo elettronico dell'Italia Nord-Orientale (Casalecchio, Bologna) with financial support from the University of Parma.

The results of the *X*-ray work are summarised in Tables 1 (atomic co-ordinates) and 2 (selected bond distances and angles), and the molecular structure is shown in the Figure.

Results and Discussion

With the aim of examining the ligand behaviour of 2,6-diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) and of comparing its spectroscopic properties in different metal complexes, we have treated the hydrazone with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} chlorides and acetates. For these latter complexes, Livingstone and Oluka [7] have recently reported the synthesis and some chemicophysical properties.

As found for the benzoyl derivative (H_2dapb),[1] H_2dapt acts as a neutral ligand with the chlorides and as a deprotonated ligand with the acetates. With the exception of the cobalt complex, which is dihydrated, nickel, copper, and zinc acetates give rise to anhydrous complexes of formula M(dapt), while tetrahydrated complexes of formula M(H_2dapt)$Cl_2\cdot4H_2O$ are formed with all the metal chlorides. The M(dapt) derivatives are less soluble in the common solvents and melt at higher temperatures than do the M(H_2dapt)$Cl_2\cdot4H_2O$ compounds (Table 3).

X-*Ray Structure of* Zn_2(dapt)$_2$.—The compound in the crystalline form exists as a dimeric species. There is a crystallographic two-fold axis normal to the four-membered Zn_2N_2 ring, whilst approximate two-fold axes pass through Zn–Zn^{I} and through C(10)–N(3)–N(3^{I})–C(10^{I}). The complex has therefore precise C_2 symmetry and approximate D_2 symmetry. Each zinc atom in the dimer is surrounded by two oxygen and two nitrogen atoms from two different ligand molecules. The four donor atoms are practically equidistant from zinc [Zn–O 2.026(6), 2.008(7) Å; Zn–N 2.020(6), 2.004(6) Å] and are approximately tetrahedrally disposed about it: the two oxygen atoms deviate upward from the best least-squares

Table 2. Selected bond distances (Å) and angles (°)

Zn–O(1^{i})	2.008(7)	S(2)–C(19)	1.685(10)	N(3)–C(12)	1.349(11)	C(12)–C(13)	1.493(10)
Zn–O(2)	2.026(6)	O(1)–C(5)	1.283(8)	N(4)–N(5)	1.388(9)	C(13)–C(14)	1.499(10)
Zn–N(2^{i})	2.004(6)	O(2)–C(15)	1.282(8)	N(4)–C(13)	1.278(11)	C(15)–C(16)	1.455(13)
Zn–N(4)	2.020(6)	N(1)–N(2)	1.403(11)	N(5)–C(15)	1.332(11)	C(16)–C(17)	1.400(16)
Zn–N(3)	2.557(6)	N(1)–C(5)	1.314(13)	C(5)–C(1)	1.471(14)	C(17)–C(18)	1.413(16)
Zn–N(3^{i})	2.599(8)	N(2)–C(6)	1.292(14)	C(6)–C(7)	1.499(11)	C(18)–C(19)	1.372(16)
S(2)–C(16)	1.706(6)	N(3)–C(8)	1.355(9)	C(6)–C(8)	1.496(13)		
O(2)–Zn–N(3)	147.7(6)	O(1^{i})–Zn–N(2^{i})	79.3(5)	N(5)–N(4)–C(13)	119.3(6)	N(4)–C(13)–C(12)	115.1(7)
O(2)–Zn–N(4)	79.1(3)	O(1^{i})–Zn–N(3^{i})	149.4(6)	N(4)–N(5)–C(15)	109.6(5)	C(12)–C(13)–C(14)	121.4(8)
O(2)–Zn–O(1^{i})	114.4(5)	N(2^{i})–Zn–N(3^{i})	70.4(4)	O(1)–C(5)–N(1)	127.8(7)	N(4)–C(13)–C(14)	123.4(8)
O(2)–Zn–N(2^{i})	111.3(5)	C(16)–S(2)–C(19)	92.6(6)	N(1)–C(5)–C(1)	115.7(6)	O(2)–C(15)–N(5)	126.3(7)
O(2)–Zn–N(3^{i})	81.4(3)	C(5)–O(1)–Zn^{i}	109.0(4)	O(1)–C(5)–C(1)	116.6(6)	N(5)–C(15)–C(16)	115.9(6)
N(3)–Zn–N(4)	70.2(3)	Zn–O(2)–C(15)	109.5(5)	N(2)–C(6)–C(8)	114.0(6)	O(2)–C(15)–C(16)	117.7(7)
N(3)–Zn–O(1^{i})	86.2(3)	N(2)–N(1)–C(5)	108.3(5)	N(2)–C(6)–C(7)	124.4(7)	S(2)–C(16)–C(15)	122.7(6)
N(3)–Zn–N(2^{i})	96.2(4)	N(1)–N(2)–Zn^{i}	114.4(4)	C(7)–C(6)–C(8)	121.6(7)	C(15)–C(16)–C(17)	125.9(6)
N(3)–Zn–N(3^{i})	92.9(5)	N(1)–N(2)–C(6)	118.7(5)	N(3)–C(8)–C(6)	115.9(8)	S(2)–C(16)–C(17)	111.1(6)
N(4)–Zn–O(1^{i})	110.2(5)	C(6)–N(2)–Zn^{i}	126.8(5)	C(6)–C(8)–C(9)	121.8(7)	C(16)–C(17)–C(18)	111.3(8)
N(4)–Zn–N(2^{i})	162.2(6)	Zn–N(4)–C(13)	126.2(5)	C(11)–C(12)–C(13)	122.6(7)	C(17)–C(18)–C(19)	112.7(10)
N(4)–Zn–N(3^{i})	98.1(5)	Zn–N(4)–N(5)	114.5(5)	N(3)–C(12)–C(13)	115.3(8)	S(2)–C(19)–C(18)	112.2(9)

Superscript i = $1 - x, y, \frac{1}{2} - z$.

Table 3. Physical and i.r. spectroscopic data (cm^{-1}) for H_2dapt, M(H_2dapt)Cl_2·$4H_2O$, and M(dapt)

	H_2dapt	M(H_2dapt)Cl_2·$4H_2O$			M(dapt)			
		Co	Ni	Zn	Co	Ni	Cu	Zn
Colour	Pale yellow	Orange	Green-yellow	Yellow	Orange-red	Dark brown	Brown	Yellow
M.p./°C	222	>305	230 (decomp.)	250 (decomp.)	>305	>305	295	285
ν(OH)		3 500ms 3 390 (sh)	3 450m	3 480m				
ν(OH)		3 300m	3 260 (sh)	3 300w	3 300m br			
ν(NH)	3 160ms	3 200 (sh)	3 170m	3 180m				
	1 695ms		1 695w	1 695mw				
	1 655 (sh)		1 655 (sh)					
Amide I	1 640vs,br	1 620vs,br	1 640vs,br	1 640vs,br				1 610w
					1 580mw	1 585mw	1 580mw	1 580mw
Ring	1 570ms	1 590 (sh)	1 560m	1 565m	1 560mw			1 560mw
					1 550mw	1 550mw	1 550mw	1 550mw
Amide II, ν(CN)	1 515ms	1 520vs,br	1 525s	1 525s	1 525s	1 525s	1 525s	1 525s
δ(CH)(aryl)		1 490s	1 490ms	1 490ms	1 490vs	1 480vs	1 480vs	1 480vs
	1 445m	1 450w	1 445 (sh)	1 445 (sh)		1 440 (sh)	1 440 (sh)	1 450m
δ(CH)(alkyl)	1 410s	1 410s	1 415s	1 420s	1 415vs	1 425vs	1 425vs	1 425vs
Amide III, ν(CN)	1 315ms	1 290s	1 280vs,br	1 290vs,br	1 325vs	1 315vs	1 315s	1 315s

plane by *ca.* 0.55 Å, while the two nitrogens deviate downward by *ca.* 0.85 Å. The metal atom is 0.53 Å above that plane. The severely distorted octahedral co-ordination at zinc is completed by two pyridine nitrogen atoms at distances of 2.557(6) and 2.599(8) Å. Thus the dimer is made up of two octahedra which are joined at a common edge with the two bridging pyridine nitrogens equally shared between the two zinc atoms. Most bond angles at zinc depart considerably from the ideal 90 and 180°. The metal · · · metal approach within the dimer is 3.551(2) Å.

The most interesting feature of the structure pertains to the unusual ligand behaviour of the pyridine ring which functions as a bridge linking two zinc atoms to form the dimer. We note, however, that such a behaviour is not a novelty having been found by Wester and Palenik[8] in the dimer $Zn_2(dapp)_2$ [H_2dapp = 2,6-diacetylpyridine bis(2′-pyridylhydrazone)]. In this compound the zinc atom exhibits an analogous distorted octahedral co-ordination, the bonds it makes with the pyridine nitrogens being considerably longer than the remaining four.

The hydrazone is deprotonated and acts as an ONNNO ligand with the pyridine nitrogen bridging two zinc atoms, giving rise to two Zn–O–C–N–N and to two Zn–N–C–C–N five-membered chelate rings. The Zn–O–C–N–N rings are nearly planar, the atoms within each ring do not deviate by more than 0.08 Å from the respective plane. Greater distortion from planarity occurs in the Zn–N–C–C–N rings, in which the largest displacement of any atom from the corresponding least-squares plane is 0.33 Å. In each of these rings the two nitrogen atoms lie at the opposite side with respect to the other three atoms. The dihedral angles between the two associated chelation rings are 7.6° [Zn–O(1)–C(5)–N(1)–N(2) and Zn–N(2)–C(6)–C(8)–N(3)] and 10.6° [Zn–O(2)–C(15)–N(5)–N(4) and Zn–N(4)–C(13)–C(12)–N(3)]. The atoms belonging to the hydrazone side-arms, including the thenoyl moiety, are not coplanar; none of them, however, is displaced more than 0.23 Å [S(1) to C(7)] or 0.33 Å [S(2) to C(14)] out of the respective least-squares plane. The side-chains are twisted by considerably large amounts, 42.1 and 31.4°, out of the plane of the central pyridine ring and are inclined

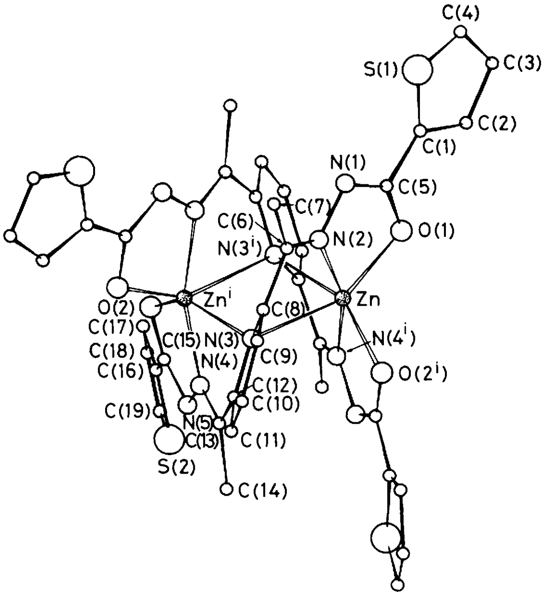

Figure. Perspective drawing of the dimeric zinc complex together with the atomic numbering. The disorder in the S(1)–C(1)–C(2)–C(3)–C(4) ring is not shown, for clarity

about 60° to each other. The lack of planarity of the hydrazone is obviously related to its co-ordinating behaviour. Although there are no H_2dapt complexes available for comparison, nevertheless it is of interest to compare the N=C–C=N–N–C(O) system in this compound with the closely related H_2-dapb[1] and 2,6-diacetylpyridine bis(picolinoylhydrazone) (H_2dappc)[2,4] derivatives. While most structural parameters are not particularly noteworthy, being similar in the different compounds, some important differences occur in the N–C–O group, for which a higher π delocalization is observed when it is deprotonated. The two thiophene rings are highly planar, with no atom deviating from the respective plane by more than 0.02 Å. These rings are slightly differently twisted with respect to the chelation ring to which they are attached, the angles of twist being 5.1 and 17.5°. Bond distances and angles in the S(2)–C(16)–C(17)–C(18)–C(19) ring appear to be normal and are in accord with those in related structures,[9] while a low degree of reliability, as a result of the disorder, is shown by the S(1)–C(1)–C(2)–C(3)–C(4) ring.

The Zn–N(3)–Zn^i–N(3^i) rhombus is nearly planar and almost perpendicular to the planes of the side-chains (89.6 and 85.5°).

The dimers contain many van der Waals interactions; the closest intermolecular contact, C(14) $\cdots$ O(1) ($x, -y, \frac{1}{2} + z$), is a distance of 3.33(1) Å.

I.r. Spectra.—The main vibrational bands of H_2dapt, $M(H_2dapt)Cl_2\cdot4H_2O$, and M(dapt) are listed in Table 3 together with the relative assignments. Unlike the H_2dapt complexes for which the N–H stretching modes are difficult to assign, due to the water molecules absorptions, the disappearance of ν(NH) bands is well evident in the anhydrous complexes as a consequence of the deprotonated nature of the ligand. Despite the hydration present, there is a striking resemblance between the i.r. spectrum of $Co(dapt)\cdot2H_2O$ and those of M(dapt) (M = Ni, Cu, or Zn), suggesting a similar co-ordinating behaviour of dapt^{2-} in all these compounds.

A comparison between the main vibrational bands of the amide group[10–13] of the hydrazone in its free and co-ordinated state leads to the following considerations. (*a*) In the $M(H_2dapt)Cl_2\cdot4H_2O$ complexes the 'amide I' band, ν(CO), decreases in the cobalt complex, while is almost unchanged in the nickel and zinc derivatives; the 'amide II' band, δ(NH) + ν(CN), increases (Δν = 10—15 cm^{-1}) in all the complexes. (*b*) In the M(dapt) complexes a strong negative shift of the 'amide I' band (Δν ≃ 60 cm^{-1}) is observed in all the complexes as a consequence of the deprotonated nature of the ligand and of the co-ordination to metal; a strong band appears at 1 525 cm^{-1} which can be attributed to the ν(CN) absorption.

Examination of the i.r. spectra of the title compounds and comparison with those of similar complexes, which we have previously examined,[1,4] reveal that in the $M(H_2dapt)Cl_2\cdot4H_2O$ derivatives the hydrazone seems to act as an ONNNO chelating agent giving rise to probable seven-co-ordination, the chloride anions and/or the water molecules being also involved in co-ordination to metal. The almost analogous spectroscopic pattern shown by the i.r. spectra of the zinc, nickel, and copper complexes suggests the same ligand behaviour for dapt^{2-} as found by *X*-ray analysis for the zinc compound.

In the metal complexes so far examined by *X*-ray diffraction the aroylhydrazone of 2,6-diacetylpyridine acts always as a planar quinquedentate ONNNO ligand,[1–4] with the only exception of $Cu_2(dappc)Cl_2\cdot H_2O$[14] in which the polydentate ligand has been found to bind two different metal atoms through seven nitrogen atoms and one oxygen atom. The ligand behaviour of the hydrazone, as found in the title compound, is further evidence for the versatility of chelation of this type of ligand.

References

1 Part 3, C. Lorenzini, C. Pelizzi, G. Pelizzi, and G. Predieri, *J. Chem. Soc., Dalton Trans.*, 1983, 721.
2 M. Nardelli, C. Pelizzi, and G. Pelizzi, *Transition Met. Chem.*, 1977, **2**, 35.
3 C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1980, 1970.
4 C. Pelizzi, G. Pelizzi, G. Predieri, and S. Resola, *J. Chem. Soc., Dalton Trans.*, 1982, 1349.
5 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.
6 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.
7 S. E. Livingstone and J. E. Oluka, *Transition Met. Chem.*, 1980, **5**, 77.
8 D. Wester and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 755.
9 W. R. Harshbarger and S. H. Bauer, *Acta Crystallogr., Sect. B*, 1970, **26**, 1010; M. D. Glick and R. E. Cook, *ibid.*, 1972, **28**, 1336; D. Zobel and G. Ruban, *ibid.*, 1978, **34**, 1652.
10 K. K. Narang and A. Aggarwal, *Inorg. Chim. Acta*, 1974, **9**, 137.
11 M. P. Teotia, J. N. Gurtu, and V. B. Rana, *J. Inorg. Nucl. Chem.*, 1980, **42**, 821.
12 R. L. Dutta and A. K. Sarkar, *J. Inorg. Nucl. Chem.*, 1981, **43**, 57.
13 M. F. Iskander, L. El-Sayed, and S. Saddeck, *Transition Met. Chem.*, 1981, **6**, 27.
14 A. Mangia, C. Pelizzi, and G. Pelizzi, *Acta Crystallogr., Sect. B*, 1974, **30**, 2146.

Received 2*nd December* 1982; *Paper* 2/2018