Comparative Study of the Structures of α-Bis(N-methylsalicylaldiminato)M^{II} (M = Ni, Cu, Pd)*

BY W. STEURER AND W. ADLHART†

Institut für Kristallographie und Mineralogie der Universität Munchen, Theresienstrasse 41, 8000 *München* 2, *Federal Republic of Germany*

Abstract

The structure of the orthorhombic high-temperature phase A [$T > 305$ (2) K] and the average structure of the incommensurate modulated phase B [305 (2) $> T > 241$ (2) K] of the Cu complex, [Cu($C_8H_8NO)_2$], (α-CuNSal), and the structure of the monoclinic phase C of the Pd complex, [Pd($C_8H_8NO)_2$], (α-PdNSal), were determined by single-crystal X-ray methods at 320, 270 K and room temperature, respectively. A: $Iba2$, $Z = 4$, $a = 9.172$ (3), $b = 24.485$ (8), $c = 6.662$ (3) Å, $U = 1496$ Å^3, $D_x = 1.45$ Mg m^{-3}, $R = 0.151$, $R_w = 0.033$ for 1601 independent reflexions. B: $Iba2$, $Z = 4$, $a = 9.17$ (3), $b = 24.59$ (11), $c = 6.59$ (2) Å, $U = 1486$ Å^3, $D_x = 1.46$ Mg m^{-3}, $R = 0.101$, $R_w = 0.053$ for 1751 independent reflexions. C: $I2/c$, $Z = 4$, $a = 9.203$ (3), $b = 24.808$ (9), $c = 6.566$ (4) Å, $\beta = 93.82$ (4)°, $D_x = 1.66$ Mg m^{-3}, $R = 0.095$, $R_w = 0.028$ for 2108 independent reflexions. A comparison between the isotypic Ni, Cu and Pd complexes indicates that the main influence on the transition temperatures of the different compounds stems from steric interactions between the molecular stacks.

Introduction

The different complexes of the title compound (α-MNSal) have been the subject of many studies during the last twenty years [for a review see Steurer & Adlhart (1983*a,b*), which will be referred to as parts I and II in the following]. This interest is due to the fact that there exist incommensurate modulated phases for α-NiNSal and α-CuNSal. For α-PdNSal only a commensurate monoclinic phase could be found.

As was pointed out in part I, the Cu and Pd phases are isotypic with the corresponding Ni phases. Attempts to prepare isotypic Fe, Co and Pt complexes failed. The main intention of this comparative study

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*IUPAC names: α-bis(N-methylsalicylideneaminato)nickel(II), etc.

† Present address: Lauerstrasse 9, 633 Wetzlar, Federal Republic of Germany.

was to elucidate the mechanism of the orthorhombic–monoclinic phase transition by investigating the influence of the central ion upon the transition temperature. A prerequisite for that was the determination or redetermination of the structures of all phases.

Experimental

Green, needle-shaped crystals of α-CuNSal and α-PdNSal (needle axis parallel to **c**) were obtained according to the method reported by Adlhart & Syal (1981). Data collection for A: Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, lattice parameters from least-squares refinement of 25 high-angle reflexions. $\Omega/2\theta$ scans in the position of minimal absorption by rotating around the scattering vector, 2546 reflexions (hkl, $\bar{h}k\bar{l}$) with $\theta < 30°$. No significant change in the intensity of one standard reflexion measured every 90 min, three orientation-control reflexions measured every 25 collected intensities. A simple heating system, blowing hot air from a distance of 1 mm to the crystal, was used. The temperature control was maintained by a Pt/Pt–10% Rh thermocouple and a digital temperature controller (DTC2, Oxford Instruments). The absolute temperature was calibrated on the phase-transition temperature at 305 (2) K. The relative temperature deviations, measured with a thermocouple at the site of the crystal, were smaller than ±2 K. Lorentz and polarization corrections in the usual way, no absorption correction [crystal diameter 0.2 mm, μ(Mo $K\alpha$) = 14.2 cm^{-1}], 1601 averaged reflexions ($R_i = 0.016$). B: Automatic Weissenberg diffractometer (AWD) controlled by an LSI-11/23 computer, 12 kW rotating anode (Rigaku), Mo $K\alpha_1$ radiation, focusing quartz monochromator. For a detailed description of the X-ray equipment, the low-temperature apparatus and the modus of data collection see part I. 4573 reflexions with $I > 0$ ($-12 \leq h \leq 12$, $-18 \leq k \leq 18$, $-8 \leq l \leq 8$), Lorentz and polarization correction (see part I), no absorption correction. 1751 averaged reflexions ($R_i = 0.030$). C: Enraf–Nonius CAD-4 four-circle diffractometer, data

collection as for A without heating. 4918 reflexions from four octants, $\theta < 35°$, Lorentz and polarization correction in the usual way, no absorption correction [crystal diameter 0·25 mm, μ(Mo $K\alpha$) = 11·9 cm^{-1}]. 2108 averaged reflexions (R_I = 0·022). The crystal was twinned [twin plane (100)]; the twin reflexions coincided for the layer l = 0. From the intensities of the twin reflexions of higher layers it was found that the twin individuals were equal and therefore the intensities of the layer l = 0 had to be halved [$I(hk0)$ = $I(\bar{h}k0)$]. All reflexions with $I > 0$ were classified as observed; weights assigned to the reflexions: w = $1/\sigma^2(F_o)$. The averaging of the intensity data and the structure refinements were performed using the program $SHELX76$ (Sheldrick, 1976) on a Cyber 170 computer. Atomic scattering factors and anomalous-dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974).

Structure refinements

The systematic extinctions hkl: $h + k + l = 2n + 1$, $h0l$: $h = 2n + 1$ and $0kl$: $k = 2n + 1$ for A and the main reflexions of B suggest the space groups $Iba2$ or $Ibam$, respectively. For C the systematic absences hkl: $h + k + l = 2n + 1$ and $h0l$: $h = 2n + 1$ indicate the possible space groups Ic or $I2/c$, respectively. The non-standard setting was chosen to demonstrate the great structural similarities to all phases of the corresponding Ni and Cu compounds. The standard setting Cc or $C2/c$ can be obtained by transforming the lattice constants and indices with the matrix $10\bar{1}/010/001$ and the coordinates with the matrix $100/010/\bar{1}01$.

The structure refinements were performed in both the centrosymmetric and the non-centrosymmetric space groups. An empirical isotropic extinction parameter g was refined, where the calculated structure factor became $F'_c = F_c(1 - 0·0001\ g\ F_c^2/\sin\ \theta)$ (Sheldrick, 1976). The positional parameters of the corresponding Ni phases (see part I) were used as a starting set. The refinements were carried out with anisotropic temperature factors for all non-hydrogen atoms, the positional parameters of the H atoms being tied to the corresponding C atoms. The temperature factors of the H atoms were refined isotropically. Hamilton (1965) tests showed the refinements in the non-centrosymmetric space groups to be significantly better ($A: R_w^{Ibam}/R_w^{Iba2}$ = 1·113, $\mathcal{R}_{30,1495,0·005}$ = 1·018; $B: R_w^{Ibam}/R_w^{Iba2}$ = 1·373, $\mathcal{R}_{30,1645,0·005}$ = 1·016; $C: R_w^{I2/c}/R_w^{Ic}$ = 1·048, $\mathcal{R}_{100,3925,0·005}$ = 1·017). However, there are very strong correlations between the atoms of the half molecules of C and thus many calculated bond lengths were chemically not reasonable. Therefore, only the results of the refinement in $I2/c$ are discussed for C. A small damping factor was necessary to avoid oscillation around the R-factor minimum when refining B.

Results and discussion

The atomic parameters of the structures A, B and C are listed in Table 1.* The positional parameters of the three phases are quite similar. The U_{33} components of the anisotropic temperature factors are for A and B much higher than the other components [e.g. for Cu^{II} in A: U_{11} = 0·0628 (4), U_{22} = 0·0614 (4), U_{33} = 0·1263 (7) Å^2] and increase even more when cooled to 270 K while U_{11} and U_{22} are reduced by the expected extent [e.g. for Cu^{II} in B: U_{11} = 0·0456 (2), U_{22} = 0·0378 (6), U_{33} = 0·1493 (5) Å^2]. The U_{33} values are about two times higher than for the corresponding Ni compound [e.g. for C(3) in A: U_{33} = 0·2575 (91) Å^2 and for C(3) in the corresponding Ni phase: U_{33} = 0·1195 (62) Å^2, see part I]. Owing to these very high temperature factors, there are many weak reflexions for higher $\sin\ \theta/\lambda$ values and this may be the reason for deviations in the determination of some bond distances.* The U_{33} values for α-PdNSal also are

Table 1. *Fractional atomic coordinates and temperature factors* (Å^2) *with e.s.d.'s in parentheses for all non-hydrogen atoms*

The values for A are given in the first, for B in the second and for C in the third line.

	x	y	z	$(U_{11} + U_{22})/2$	U_{33}
Cu	0	0	0	0·0621 (4)	0·1263 (7)
	0	0	0	0·0417 (4)	0·1493 (5)
Pd	0	0	0	0·0371 (2)	0·0464 (3)
N	−0·1251 (4)	0·0653 (2)	−0·011 (3)	0·066 (3)	0·126 (6)
	−0·1245 (2)	0·0668 (1)	−0·010 (1)	0·037 (2)	0·141 (2)
	−0·1276 (3)	0·0655 (1)	−0·0114 (7)	0·039 (2)	0·048 (3)
O	0·1695 (3)	0·0430 (1)	−0·008 (2)	0·064 (2)	0·200 (5)
	0·1697 (2)	0·0426 (1)	−0·006 (1)	0·049 (2)	0·211 (2)
	0·1787 (3)	0·0446 (1)	0·0185 (6)	0·039 (2)	0·075 (3)
C(1)	0·1861 (7)	0·0958 (2)	−0·008 (4)	0·076 (4)	0·129 (8)
	0·1863 (3)	0·0952 (2)	−0·004 (1)	0·072 (2)	0·134 (2)
	0·1883 (5)	0·0972 (2)	0·0162 (9)	0·054 (3)	0·045 (4)
C(2)	0·3286 (6)	0·1167 (2)	−0·004 (4)	0·076 (3)	0·205 (8)
	0·3279 (4)	0·1167 (2)	0·004 (1)	0·052 (2)	0·196 (2)
	0·3298 (4)	0·1203 (2)	0·0262 (9)	0·050 (3)	0·079 (4)
C(3)	0·3503 (6)	0·1723 (2)	0·005 (4)	0·092 (4)	0·258 (9)
	0·3533 (4)	0·1694 (2)	−0·007 (1)	0·069 (2)	0·176 (2)
	0·3489 (5)	0·1746 (2)	0·022 (1)	0·068 (3)	0·100 (6)
C(4)	0·2378 (7)	0·2079 (2)	−0·012 (3)	0·098 (4)	0·166 (8)
	0·2394 (4)	0·2074 (2)	0·005 (1)	0·060 (2)	0·202 (2)
	0·2315 (6)	0·2093 (2)	0·009 (1)	0·072 (4)	0·103 (6)
C(5)	0·0978 (6)	0·1886 (2)	−0·004 (3)	0·086 (3)	0·150 (7)
	0·0982 (3)	0·1865 (2)	0·001 (1)	0·069 (2)	0·146 (2)
	0·0946 (5)	0·1881 (2)	0·001 (1)	0·059 (3)	0·079 (5)
C(6)	0·0695 (8)	0·1325 (2)	−0·018 (3)	0·083 (4)	0·120 (9)
	0·0717 (3)	0·1327 (2)	−0·006 (1)	0·047 (2)	0·121 (2)
	0·0690 (7)	0·1325 (2)	0·004 (1)	0·055 (3)	0·047 (4)
C(7)	−0·0797 (7)	0·1154 (2)	0·014 (3)	0·070 (4)	0·086 (8)
	−0·0816 (3)	0·1154 (2)	0·012 (1)	0·049 (2)	0·134 (2)
	−0·0819 (6)	0·1143 (2)	−0·008 (1)	0·048 (3)	0·046 (4)
C(8)	−0·2877 (5)	0·0573 (2)	−0·029 (3)	0·082 (4)	0·144 (10)
	−0·2890 (3)	0·0597 (2)	−0·029 (1)	0·061 (2)	0·151 (2)
	−0·2893 (4)	0·0583 (2)	−0·026 (1)	0·048 (3)	0·071 (4)

substantially higher than U_{11} or U_{22} for some atoms [e.g. for C(3): $U_{11} = 0.069$ (3), $U_{22} = 0.068$ (3) and $U_{33} = 0.100$ (6) Å^2].

The results* of a thermal-motion analysis (TLS) (Schomaker & Trueblood, 1968), calculated with XANADU (Roberts & Sheldrick, 1976), indicate the existence of a main libration axis parallel to **b** and a main translation direction parallel to **c** (for A and B only). The values for the translation and libration terms for A and B are much higher than for the corresponding Ni phases [α-CuNSal: A: $L_{22} = 0.007$ (2)

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* See deposition footnote.

Table 2. *Lattice parameters of the isotypic compounds* α-NiNSal, α-CuNSal *and* α-PdNSal *at various temperatures*

The ionic radii for Ni^{II}, Cu^{II} and Pd^{II} are 0.72, 0.69 and 0.82 Å, respectively.

Temperature (K) (RT = room temperature)	a (Å)	b (Å)	c (Å)	β (°)	M in α-M-NSal
320	9.172 (2)	24.485 (8)	6.662 (3)	90	Cu
RT	9.167 (2)	24.282 (4)	6.597 (1)	90	Ni*
RT	9.197 (3)	24.55 (1)	6.635 (2)	90	Cu
RT	9.203 (3)	24.808 (9)	6.566 (4)	93.82 (4)	Pd
270	9.17 (3)	24.59 (11)	6.59 (2)	90	Cu
237	9.119 (2)	24.555 (5)	6.574 (2)	93.06 (3)	Cu†
190	9.16 (1)	24.54 (3)	6.55 (1)	94.2	Cu†
160	9.09 (3)	24.13 (2)	6.43 (2)	90	Ni*
145	9.13 (5)	24.10 (13)	6.45 (1)	92.7 (1)	Ni*
40	9.15 (3)	24.22 (8)	6.41 (3)	93.9 (1)	Ni*

* Part I.
† Adlhart & Syal (1981).

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rad^2, $T_{33} = 0.118$ (9) Å^2; B: $L_{22} = 0.003$ (2) rad^2, $T_{33} = 0.139$ (8) Å^2 and for α-NiNSal:A:$L_{22} = 0.002$ (1) rad^2, $T_{33} = 0.050$ (5) Å^2; B: $L_{22} = 0.0046$ (8) rad^2, $T_{33} = 0.076$ (4) Å^2].

The calculations for the half molecules of B and C reveal the formation of a new libration axis parallel to **a** which can be interpreted as a kind of 'fluttering' motion of the molecule. The translation tensor for C is rather isotropic.

Table 2 gives the cell parameters of all the investigated phases of the three isotypic compounds. Evidently the ionic radius has a pronounced influence on the lattice constant b, whereas c is essentially determined by the van der Waals radius of the benzene ring. The bond lengths M^{II}–N and M^{II}–O increase from $M = $ Ni to $M = $ Pd and so do the lengths of the molecules causing a slightly different packing. To demonstrate this behaviour sections of the crystal structures of the room-temperature phase of the Ni compound and of A and C are shown in Fig. 1. The angle between the longitudinal axes of molecules lying above one another decreases from the Ni to the Pd complex, which is easily seen by looking at the position of the H(C5) atom. In the same sequence the overlap of the H(C4) atoms of adjacent molecule stacks increases. This may be one important factor for the extent of the rigidity of the structures. α-NiNSal, with the weakest steric interaction between the molecule stacks, has the lowest transition temperature. The amplitude of the modulation wave near the transition temperature of about 5% of c is lower than for α-CuNSal (about 7% of c) and consequently the
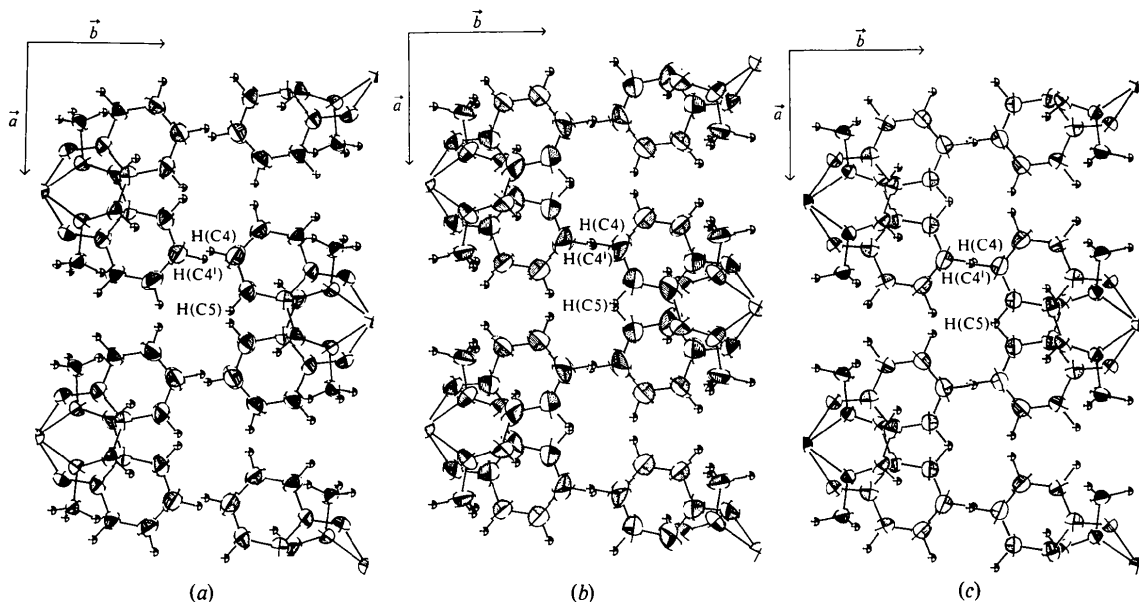

(a)   (b)   (c)

Fig. 1. Sections of the crystal structures of (a) α-NiNSal at room temperature, (b) α-CuNSal at 320 K and (c) α-PdNSal at room temperature. The plots are projections down **c**; the probability level of the thermal ellipsoids is 50%; the radii of the H atoms are set to 0.1 Å. (ORTEP, Johnson, 1965.)

monoclinic angle of the low-temperature phase for α-NiNSal is smaller than for α-CuNSal (see Table 2). α-PdNSal has the strongest steric interactions and exists only in the monoclinic phase.

Besides the steric interactions between the structure-building elements (the rigid molecule stacks) there are other factors influencing the transition temperatures, such as the different atomic masses of Ni and Cu on the one hand and of Pd on the other, or the fact that there exists an $s = \frac{1}{2}$ spin system for the Cu^{II} compound (Bartowski & Morosin, 1972).

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The Structure of the Incommensurate Modulated Phase of α-Bis(N-methylsalicylaldiminato)copper(II)*

BY W. STEURER AND W. ADLHART†

Institut für Kristallographie und Mineralogie der Universität München, Theresienstrasse 41, 8000 München 2, Federal Republic of Germany

Abstract

The modulated structure of the title compound [α-CuNSal, $Cu(C_8H_8NO)_2$] was determined at 270 K by single-crystal X-ray methods. The refinements were performed in the superspace group $P^{I\bar{b}a\bar{2}}_{1\bar{1}\bar{1}}$ (α00) considering fluctuations in phase and amplitude, respectively, of the static modulation wave. Final overall R factors $R = 0.176$ and $R_w = 0.065$ were obtained for 8338 independent reflexions (with $I > 0$) including 3542 first- and 3046 second-order satellite reflexions. The modulation waves are sinusoidal with main displacements parallel to c and small longitudinal components parallel to a. The phason factors were found to be comparable to the normal Debye–Waller factors with high values for the atoms around the central Cu^{II} ion and small values for the peripheral atoms, thus showing the same tendency as the amplitudes. The results are comparable to those for the isotypic modulated structure of the corresponding Ni compound.

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* IUPAC name: α-bis(N-methylsalicylideneaminato)copper(II).
† Present address: Lauerstrasse 9, 633 Wetzlar, Federal Republic of Germany.

Introduction

Recently the incommensurate modulated structure of α-CuNSal [305 (2) > T > 241 (2) K] has been the subject of a study (Adlhart, Blank & Jagodzinski, 1982) in which the authors explained the intense diffuse scattering around the satellite reflexions by phase fluctuations of the static displacement wave. In order to obtain reliable proof for this assumption from the Bragg reflexions, a refinement of the modulated structure taking into account a phason factor was performed in a similar way as for the isotypic modulated structure of α-NiSal (Steurer & Adlhart, 1983a; hereafter referred to as part I).

Experimental

The preparation of the crystal, the modus of data collecting and the data reduction were described in Steurer & Adlhart (1983b; part II hereafter).

20 542 reflexions out of 26 992 measured main, first- and second-order satellite reflexions had intensities greater than zero and were classified as observed. Considering anomalous dispersion the equations