Inorganica Chimica Acta, 122 (1986) 129–133

Synthesis of Mixed Sphere β-Diketonate Nickel(II) Complexes

G. FAVERO*, B. CORAIN*, M. BASATO and S. ISSA**

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., c/o Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35100 Padua, Italy

(Received April 30, 1986; revised July 22, 1986)

Abstract

Complexes of the type [Ni(β-diketonate)(L–L)$_{1,2}$] (L–L = diphosphine, (**2**), en or dipy, (**3**)) have been synthesized from [Ni(β-diketonate)$_2$] (**1**) and the free ligand under stoichiometric conditions in ethanol. Complexes **2** are square-planar species, while compounds **3** are hexacoordinate complexes, all being quite stable toward ligand disproportionation. The ligand-set $\{P_2O_2^-\}$ appears to be particularly stable in the nickel(II) coordination sphere and turns out to exert a fairly strong average ligand field.

Introduction

Homoleptic β-carbonylenolate metal complexes have been known and thoroughly investigated for a long time, starting from 1887 [1]. In contrast with extensive studies on their physico-chemical and structural properties as well as on their analytical applications, comparatively little attention was focused on the chemistry of the metal-β-carbonylenolate ring, which can be considered a strong metallo-organic nucleophile, potentially useful for organic syntheses.

Thus, apart from the extensive work carried out in the sixties [1] (mainly by Collman and coworkers and by Singh and Sahai) primarily on substitution reactions of the methino hydrogen atom by electrophiles, further exploitation of the organic chemistry of the ring appears to have been pursued only rather recently in these [2] and other [3] laboratories.

With the aim to 'tune' the reactivity of the β-carbonylenolate nucleophile by proper changes in the remainder of the coordination sphere of the metal, we started to systematically explore [4] the possibility of preparing novel heteroleptic* β-carbonylenolate complexes related to the catalytically active homoleptic ones [2, 3].

Results

We focused our attention on nickel(II), *i.e.* a borderline metal centre and we utilized some phosphorus and nitrogen donors as heteroligands.

The starting compounds were typical 'octahedral' (*vide infra*) trimeric bis(β-diketonate) nickel(II) complexes such as [Ni(acac)$_2$], [Ni(ba)$_2$] (ba = benzoylacetonate) and [Ni(dbm)$_2$] (dbm = dibenzoylmethanate). The general synthetic approach is depicted as follows

$$[\mathrm{Ni(O{-}O)_2}] + n\mathrm{L{-}L} \xrightarrow[\mathrm{EtOH}]{+\,\mathrm{NaBPh_4},\ -\,\mathrm{Na(O{-}O)}} [\mathrm{Ni(O{-}O)(L{-}L)}_n]\mathrm{BPh_4}$$

O–O = β-diketonate; L–L = diphosphine (n = 1, compounds **2**) or en, dipy (n = 2, compounds **3**).

Compounds **2** and **3** are obtained in fair to good yields (Table I). They are appreciably soluble in polar solvents and behave as uniunivalent weak electrolytes in acetone ($(\Lambda_e)_\infty$ = 100–120 Ω^{-1} cm^2 eq^{-1}).

O,O′-bonded heteroleptic complexes are relatively less common than their homoleptic or 'pseudoheteroleptic'† analogs and the most investigated metal centers are, in this respect, Co^{III} [5], Ni^{II} [6], Cu^{II} [7], Pd^{II} [8], Pt^{II} [9]. To our knowledge, only two examples of O,O′-bonded heteroleptic phosphine complexes were known as isolated species [10] at the beginning of this research, *i.e.* [Pt(acac)(PPh$_3$)$_2$]$^+$ and [Pd(tfacac)(PCy$_3$)$_2$]$^+$ (tfacac = trifluoroacetylacetonate) which had been prepared by reaction of free phosphine to [Pt(tfacac)(acac)] and to [Pd(tfacac)$_2$] respectively in aprotic solvents.

---

*Authors to whom correspondence should be addressed.

**On leave of absence from Faculty of Industrial Chemistry, Somali National University, P.O. Box 1081, Mogadishu, Somalia.

*With this term we wish to indicate complexes having at least one β-carbonylenolate ligand in the coordination sphere.

†We propose this term for indicating complexes containing only β-diketonate ligands, but not all identical to each other.

0020-1693/86/$3.50

TABLE I. Novel [Ni(β-diketonate)(L–L)$_{1,2}$](BPh$_4$) Complexes

Complex^a		Analytical data^b (%)			Melting point (°C)	Color	Yield (%)
		C	H	N			
2a	[Ni(acac)(dppe)]$^+$	75.47 (75.37)	5.83 (5.84)		185	yellow	$71^{c}(53)^{d}$
2b	[Ni(acac)(dppp)]$^+$	75.88 (75.62)	6.02 (6.01)		147	yellow	79(28)
2c	[Ni(acac)(dppb)]$^+$	76.47 (75.77)	6.17 (6.14)		251	orange–yellow	74(37)
2d	[Ni(ba)(dppe)]$^+$	76.75 (76.87)	5.72 (5.70)		182	yellow	66(42)
2e	[Ni(dbm)(dppe)]$^+$	77.16 (78.10)	5.51 (5.55)		273	yellow	89(23)
2f	[Ni(dbm)(dppp)]$^+$	78.40 (78.21)	5.69 (5.67)		179	yellow	82(42)
2g	[Ni(dbm)(dppb)]$^+$	77.50 (78.31)	5.79 (5.79)		224	yellow	77(40)
3a	[Ni(acac)(en)$_2$]$^+$	66.49 (66.36)	7.54 (7.26)	9.28 (9.38)	236	mauve	66(42)
3b	[Ni(acac)(dipy)$_2$]$^+$	74.51 (74.55)	5.88 (5.49)	6.70 (7.10)	221	cream	85(61)

^{a}Dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)-butane. ^{b}Figures in parentheses are calculated values. . ^{c}Crude. ^{d}Recrystallized.

TABLE II. Selected Spectroscopic Data for the [Ni(β-diketonate)(L–L)$_{1,2}$]$^+$ Complexes

Complex	$\nu(\mathrm{C}\cdots\mathrm{O})$ and $\nu(\mathrm{C}\cdots\mathrm{C})$ (cm^{-1})^a	[Ni^{II}] (M × 10^{+3})	λ_{max} (ϵ^b) (nm) (M^{-1} cm^{-1}) in CH$_2$Cl$_2$
2a	1560, 1525	0.5–5.0	425(1740)
2b	1580, 1560, 1530	0.5	435(705)
2c	1580, 1560, 1530	1.0	450(670)
2d	1590, 1550	0.1	430(1280)
2e	1590	1.0	~430(sh) (~1500)
2f	1590	0.1	435(1140)
2g	1595	0.2	undetected^c
3a	1590	17	565(9); 775(4.5)
3b	1600	5	550(15.5); 780(6.2)

^{a}All bands are strong in intensity. ^{b}Apparent values at the indicated concentration. ^{c}Merged with the strong 360 nm charge transfer band.

On the basis of these considerations, the complexes listed in Table I represent the first well documented list of this type of tetracoordinate compounds.

The nature of O,O′ bonded β-diketonate complexes is documented by their IR spectra and by the X-ray molecular structure of **2a** very briefly reported by us [7].

Infrared Spectra

O,O′ β-Diketonate ligands display typical strong bands in the range 1650–1500 cm^{-1} due to the stretching of the $\mathrm{C}\cdots\mathrm{O}$ and $\mathrm{C}\cdots\mathrm{C}$ ring groups.

Any other coordination mode [1, 11] can be easily detected in this way and it has been ruled out without ambiguity for all the compounds reported here. The wavenumbers of the relevant bands (sometime appearing as composite absorptions) are collected in Table II, together with the spectral data in the visible range. The IR spectra of all compounds exhibit also the typical absorptions of the heteroligands.

In agreement with the structural suggestions stemming from the IR data, the X-ray molecular structure of **2a** exhibits the expected O,O′-bonded [M(β-diketonate)] ring (Fig. 1) as well as the metal-coordinated bidentate heteroligand.

The molecule is essentially planar and is slightly distorted towards the tetrahedral configuration. The Ni–P bond length is much shorter than that

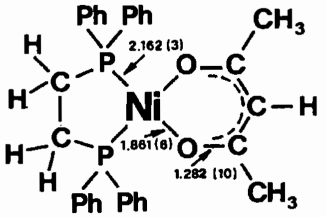

Fig. 1. Sketch of the molecular structure of **2a** (data from ref. 4, lengths in Å).

observed in *trans*-$[NiX_2(PPh_3)_2]$ molecules (d = 2.225(1) and 2.242(3) Å for X = CN [12] and Cl [13], respectively) in agreement with an expected stronger Ni^{II}–P bond, as a consequence of the lack of competition of the *trans* ligands. The Ni–O bond is slightly longer than that observed in square planar $[NiO_4]$ complexes (e.g., d = 1.836(5) in bis(dipivaloylmethanato)nickel(II)) as a consequence of a strong *trans* effect of the PPh_2R ligand moiety. Finally, the mean 1.282(10) Å figure for the C$\overline{\cdots}$O bonds is slightly lower than that observed in the above mentioned complex [14] (d = 1.314(10) average).

Visible Spectra

All compounds **2** exhibit one broad band (sometime appearing as a tail of the UV absorption) in their Vis spectra, with ϵ values ranging from 600 to 1700 M^{-1} cm^{-1}. The relevant λ_{max} figures fall in a fairly restricted spectral range, *i.e.* 425–450 nm. The spectra of **2a** obey Lambert–Beer's law in the range 5×10^{-3}–0.5 M.

Square planar nickel(II) complexes with ligand sets $\{O_4{}^{2-}\}$ such as for example bis(dipivaloylmethanate)nickel(II) display their ligand field band in the range 535–560 nm [15] and ϵ values ranging from 50 to 200 M^{-1} cm^{-1}. Moreover, $[Ni(dppe)_2]^{2+}$ exhibits the relevant band at 400 nm, in agreement with the higher ligand field strength of the $\{P_4\}$ ligand set.

On the basis of these observations, the ligand field band of the $[NiP_2O_2]^+$ complexes reported here falls in a rather unexpected range, as λ_{max} values around 450–500 nm would appear more reasonable on the basis of qualitative elementary ligand field considerations.

Also the ϵ figures for complexes **2** appear unusual for planar d^8 complexes, but they are less surprising on considering the lower symmetry of complexes **2**.

Both λ_{max} and ϵ values for complexes **3a** and **3b** appear, on the other hand, rather normal and they do not seem to deserve any particular comment, in this context.

Thermal Solid State Behaviour of Complexes 2a, 3a, 3b

It seems interesting to investigate the thermal behaviour of compounds **2** and **3** in the solid state for detecting any tendency to either allogonic transitions of compounds **2** [12] or to loss of ligands from complexes **3**. Data for **3a** and **3b** are collected in Figs. 2 and 3 and refer to experiments performed in a nitrogen atmosphere.

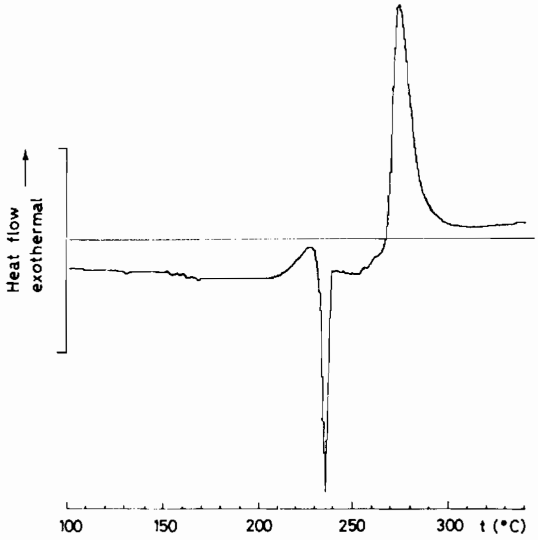

Fig. 2. DSC profile for complex **3a** (10 °C/min).

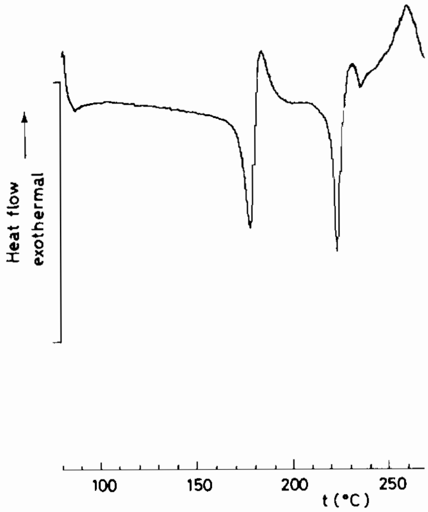

Fig. 3. DSC profile for complex **3b** (10 °C/min).

It is found that **2a** can be heated up to 180 °C without any change both in chemical composition and in physical state.

When heated up to 200 °C, **3a** displays an exothermic event (–5 kcal/mole) followed (and perhaps partially overlapped with) by the melting of the material (+7 kcal/mole). Experiments carried out at a 50 mg scale out of the instrument at 210 °C showed that the exothermic event is accompanied by a color change from mauve to dark brown ($3a_t$). The elemental analysis of $3a_t$ yielded results in fair agreement with those of **3a**. The spectrum of $3a_t$

recorded in acetone in the range 350–600 nm appears as a long tail of a strong UV band, but the features of the chromophore present in **3a** are still detectable. These results suggest that the exothermic event embodies, in fact, a polymorphic transition and a chemical reaction which does not totally destroy the 'NiO_2N_4' chromophore.

Figure 3 depicts the DSC behaviour of **3b**. It is seen that an endothermic process occurs in the 150–180 °C range (+7 kcal/mole) followed by an exothermic one between 180 and 190 °C (–5 kcal/mole). The so obtained system undergoes a further endothermic event in the range 210–225 °C. A 50 mg scale experiment performed out of the calorimeter reveals that the thermal events occurring between 150 and 190 °C correspond to the melting of cream colored **3b** followed by the immediate crystallization of the molten phase to give a dark brown microcrystalline solid (**3b**$_t$), which analyses as **3b** and melts at 222 °C. The visible spectrum of **3b**$_t$ recorded in acetone is very similar to that of **3b** in the range 600–900 nm (both in terms of spectral shape and band intensity) while in the range 400–600 nm, the 550 band present in pure **3b** appears relatively less intense (*ca.* 40%). The higher absorbance observed around 550 nm is evidently due to a partial chemical change of **3b** into an unidentified species. This seemingly minor chemical event accompanies the dimorphic transition which occurs after the melting of the room temperature stable **3b** phase.

Conclusions

The mixed soft–hard $\{P_2O_2^-\}$ coordination sphere in heteroleptic complexes [Ni(β-diketonate)(diphosphine)]$^+$ seems to be well suited for coordinating a borderline metal center like Ni^{II}. The stability of complexes **2** in solution towards, for example, ligand disproportionation appears remarkable, in this respect, and preliminary experiments [17] carried out by reacting $[Ni(acac)_2]$ with $[Ni(dppe)_2]^{2+}$ in $C_2H_4Cl_2$ show that, in fact, ligand comproportionation to give **2a** rapidly occurs.

The existence of complexes **2** in solution as planar species appears to be also remarkable. One would have expected, in fact, that, the substitution of one acac$^-$ ligand in $[Ni(acac)_2]$ by one dppe ligand would not have caused total destabilization of the exceedingly stable trimeric structure of $[Ni(acac)_2]_3$, but this has to be the consequence of the overall increase in the covalent character of the Ni–ligand bonds.

Further work relative to the solution chemistry of Ni^{II} acetylacetonate complexes in the presence of dppe is in progress in our laboratories.

Experimental

Instruments

Melting points were taken with a Kofler apparatus (Reichest Thermavar) and are uncorrected. Infrared spectra were determined by a Perkin-Elmer model 580 spectrophotometer and visible spectra by a Perkin-Elmer Lambda 5 apparatus. DSC measurements were carried out by a Mettler TA3000 calorimeter and TG analysis by a Perkin-Elmer TGS-2 thermobalance. Conductivity measurements were performed by a CDM Radiometer instrument.

Materials and Procedures

Nickel β-diketonate complexes were either commercial chemicals ($[Ni(acac)_2]$ from Merck Schuchardt) or they were prepared by literature methods [16]. Dppe and $NaBPh_4$ were Fluka and Janssen reagents, respectively and were used as received. Dppp and dppb were prepared by literature methods [17]. The synthetic work was carried out under argon.

Typical Procedure for the Synthesis of Complexes 2 and 3

Hot ethanol solutions of the requested starting complex **1** (1 mmol in 20 ml) and of the proper ligand (1 or 2 mmol in 30 ml) were mixed and kept under vigorous stirring. $NaBPh_4$ (1 mmol) dissolved in ethanol (3–4 ml) was added and compounds **2** and **3** were obtained as microcrystalline precipitates either from hot ethanol or at room temperature. They were filtered off and washed with ether (3 X 20 ml). Crude complexes **2** and **3** were often found analytically pure, but recrystallization is recommended (from acetone upon addition of ethanol). Data referring to the electrical conductivity of acetone solutions of **2** and **3** are as follows (Λ_e and Ni^{II} concentration $\times 10^{+3}$ in parentheses): **2a** (104, 5.75); **2b** (93, 5.87); **2c** (91, 5.86); **3a** (106, 7.06); **3b** (105, 6.33).

Acknowledgements

We thank Mr. A. Ravazzolo for technical assistance. This work was partially supported by 'Progetto Finalizzato Chimica Fine e Secondaria', C.N.R.

References

1 R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal β-Diketonates and Allied Derivatives', Academic Press, London, 1978.

2 (a) M. Basato, B. Corain, M. Cofler, A. C. Veronese and G. Zanotti, *J. Chem. Soc., Chem. Commun.*, 1593 (1984); (b) M. Basato, B. Corain, A. C. Veronese, F. D'Angeli, G. Valle and G. Zanotti, *J. Org. Chem.*, *49*,

4696 (1984) and refs. therein; (c) M. Basato, R. Campostrini, B. Corain, F. D'Angeli, A. C. Veronese and G. Valle, *Inorg. Chim. Acta, 98*, L17 (1985).

3 (a) K. Uehara, Y. Ohashi and M. Tanaka, *Bull. Chem. Soc. Jpn., 49*, 1447 (1976); (b) R. P. Eckberg, J. H. Nelson, J. W. Kenney, P. N. Howells and R. A. Henry, *Inorg. Chem., 16*, 3128 (1977); (c) J. H. Nelson, P. N. Howells, G. C. De Lullo and G. L. Landen, *J. Org. Chem., 45*, 1246 (1980); (d) A. Corsico Coda, G. Desimoni, P. Righetti and G. Tacconi, *Gazz. Chim. Ital., 114*, 417 (1984); (e) H. Brunner and B. Hammer, *Angew. Chem., Int. Ed. Engl., 23*, 312 (1984); (f) C. P. Fei and T. H. Chan, *Synthesis*, 467 (1982); (g) O. Attanasi, P. Bonifazi and F. Buiani, *J. Heterocyclic Chem., 20*, 1077 (1983).

4 M. Basato, B. Corain, G. Favero and G. Valle, *Z. Kristal., 167*, 153 (1984).

5 (a) T. Ohishi, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn., 56*, 3441 (1983); (b) T. Ohishi, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn., 56*, 1553 (1983); (c) K. Kashiwabara, K. Katoh, T. Ohishi, J. Fujita and M. Shibata, *Bull. Chem. Soc. Jpn., 55*, 149 (1982).

6 N. Hoshino, Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn., 54*, 420 (1981).

7 (a) T. Kogane and R. Hirota, *Bull. Chem. Soc. Jpn., 53*, 91 (1980); (b) N. A. Bailey, D. E. Fenton, M. V. Franklin and M. Hall, *J. Chem. Soc., Dalton Trans.*, 984 (1980).

8 H. Tanaka, K. Isobe, S. Kawaguchi and S. Okeya, *Bull. Chem. Soc. Jpn., 57*, 456 (1984).

9 S. Okeya, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn., 55*, 1460 (1982).

10 S. Okeya, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn., 54*, 3396 (1981).

11 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1963.

12 B. Corain, M. Basato, G. Favero, P. Rosanò and G. Valle, *Inorg. Chim. Acta, 85*, L27 (1984).

13 B. Corain, B. Longato, R. Angeletti and G. Valle, *Inorg. Chim. Acta, 104*, 15 (1985).

14 F. A. Cotton and J. J. Wise, *Inorg. Chem., 7*, 1200 (1966).

15 B. Corain, M. Basato, C. Ballotta and M. Ahmed, *Inorg. Chim. Acta, 87*, 105 (1984).

16 L. Wolf and E. Butter, *Z. Anorg. Allg. Chemie, 339*, 191 (1985).

17 S. Issea, work in progress.