Inorganica Chimica Acta, 117 (1986) 145–149

A Novel Unsymmetrical Quadridentate Ligand 1-(2'-Aminophenyl)-6-methyl-2,5-diazanona-1,6-diene-8-one and its Complexes with Copper(II), Nickel(II) and Palladium(II)

EDMUND KWIATKOWSKI and MAREK KWIATKOWSKI

Institute of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland

(Received January 24, 1986)

Abstract

Two routes for the preparation of the title compound (**6**) have been developed. Reaction of equimolar quantities of 2-aminobenzaldehyde, pentane-2,4-dione and 1,2-diaminoethane yields the ligand **6** and 2-methyl-3-acetylquinoline as side product. The compound **6** was obtained in high yield in a one-step condensation of 2-aminobenzaldehyde with 1-amino-4-methyl-3-azahept-4-ene-6-one (**5**). Studies on the condensation of **5** with various 2-aminobenzaldehyde derivatives revealed that the yield of unsymmetrical ligand is evidently influenced by the acidic properties of the hydrogen atom (or atoms) of the ring substituent in the *ortho* position to the carbonyl group. Copper(II), nickel(II) and palladium(II) complexes of **6** have been prepared and characterized. Spectroscopic data of nickel and palladium complexes are consistent with their planar structure. A superhyperfine splitting due to nitrogen is observed in the EPR spectrum of the copper complex in spite of the presence of azomethine hydrogen atom.

Introduction

In the course of our study on transition metal complexes with linear unsymmetrical quadridentate Schiff bases, we searched for a convenient method for the synthesis of such compounds. The most promising route led via the monocondensation product of pentane-2,4-dione and 1,2-diaminoethane: 1-amino-4-methyl-3-azahept-4-ene-6-one (**5**) [1, 2]. By the condensation of this intermediate with various carbonyl compounds, several quadridentate ligands of the N_2O_2 type (*i.e.*, comprising two nitrogen and two oxygen donor atoms) were obtained [1–5]. Otherwise, a survey of literature revealed that, except for one very recent paper [6] reporting the preparation of quadridentate Schiff base derived from 2-formylpyrrole, pentane-2,4-dione and 1,2-diaminoethane, analogous unsymmetrical ligands comprising a N_3O set of donor atoms were not isolated. In this work we studied two different routes for preparation of linear unsymmetrical Schiff-base ligands of the N_3O type with a primary aromatic amino-group as one of the donors. As a result, a novel unsymmetrical ligand 1-(2'-aminophenyl)-6-methyl-2,5-diazanona-1,6-diene-8-one (**6**) was obtained by the reaction of intermediate **5** with 2-aminobenzaldehyde. The potential possibilities of compound **5** for the synthesis of other N_3O type ligands were also studied. Copper(II), nickel(II) and palladium(II) complexes of ligand **6** were prepared and characterized.

Experimental

Mass spectra were recorded on Varian MAT CH5 and MS 90 A.R.I. Scientific Apparatus spectrometers at 70 eV. Proton and ^{13}C NMR spectra were obtained on Bruker WM 250 and 360 MHz spectrometers, EPR spectra on JES-ME-3X X-band spectrometer, UV and visible absorption spectra on a Perkin-Elmer UV–Vis 402 spectrometer, and IR spectra on a Specord 71 spectrometer using hexachlorobutadiene mulls. Molecular weights were determined on a Mechrolab 302 Vapour Pressure Osmometer.

Reagents

1-amino-4-methyl-3-azahept-4-ene-6-one (**5**) and 2-aminobenzaldehyde were prepared by the literature methods [1, 7].

1-(2'-aminophenyl)-6-methyl-2,5-diazanona-1,6-diene-8-one (6)

To the hot solution of freshly prepared 2-aminobenzaldehyde (1.21 g, 0.01 mol) in chloroform (50 cm^3), a solution of **5** (1.42 g, 0.01 mol) in chloroform (10 cm^3) was added. The mixture was refluxed for 2 h, then cooled, dried over anhydrous magnesium sulphate and evaporated to yield the crude ligand (**6**) in the form of a colourless oil.

0020-1693/86/$3.50

Copper complex (7)

The crude ligand (**6**) (0.01 mol) was dissolved in acetone (20 cm^3), and 1.20 g (0.005 mol) of finely powdered dicopper dihydroxide carbonate hydrate was added. The mixture was stirred at room temperature until the copper salt dissolved completely (*ca.* 3 h). The resulting dark-brown solution deposited, upon concentration, a dark solid which was recrystallized from methanol to give 7 (1.50 g) in the form of dark-brown glossy prisms, melting point (m.p.) 134 ℃; *Anal.* Calc. for $C_{14}H_{17}N_3OCu$: C, 54.79; H, 5.58; N, 13.69; Cu, 20.71; mol. wt. 306.9. Found: C, 54.68; H, 5.64; N, 13.71; Cu, 20.75%; mol. wt. 313 ($CHCl_3$).

Nickel complex (8)

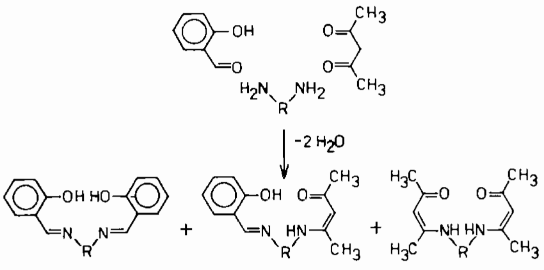
To the solution of nickel acetate tetrahydrate (2.49 g, 0.01 mol) in methanol (20 cm^3), a solution of crude ligand (**6**) (0.01 mol) in 30 cm^3 of methanol was added. The mixture was refluxed and stirred for 30 min, and then concentrated under reduced pressure until a coloured solid precipitated. The precipitate was recrystallized from the methanol–chloroform mixture to give 8 (1.20 g) in the form of red–brown needles, m.p. 179 ℃; *Anal.* Calc. for $C_{14}H_{17}N_3ONi$: C, 55.68; H, 5.67; N, 13.91; Ni, 19.37; mol. wt. 302.0. Found: C, 55.67; H, 5.65; N, 13.94; Ni, 19.41%; mol. wt. 307 ($CHCl_3$).

Palladium complex (9)

To the solution of palladium acetate (0.229 g, 0.001 mol) in acetone (10 cm^3) a solution of ligand (**6**) (0.001 mol) in acetone (20 cm^3) was added. The mixture was refluxed for 1 h and evaporated yielding a dark oil which upon standing deposited a few red–brown crystals of **9** (0.110 g), m.p. 230 ℃ decomposition; *Anal.* Calc. for $C_{14}H_{17}N_3OPd$: C, 48.08; H, 4.90; N, 12.01. Found: C, 48.00; H, 4.79; N, 12.13%.

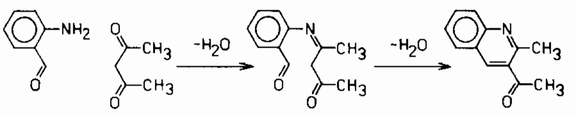
Results and Discussion

A simple reaction of equimolar quantities of 1,2-diamine, pentane-2,4-dione and an appropriate 2-hydroxycarbonyl aromatic compound (Scheme 1) followed by the isolation of unsymmetrical product **1** from the mixture with two symmetrical analogues **2** and **3** provided an effective method for the preparation of unsymmetrical quadridentate Schiff-base ligands in some cases [8–10]. However, when the 2-hydroxycarbonyl compound was replaced by 2-aminobenzaldehyde, the FD mass spectrum of the reaction mixture revealed four intense peaks. Three of them, $m/z = 245$, 266 and 224, corresponded to quadridentate ligands analogous to unsymmetrical **1** and two symmetrical **2** and **3**, respectively. The fourth peak appeared at $m/z = 185$, and indicated the formation of an additional byproduct. This product could be isolated from the reaction mixture in the form of yellow needles and was identified as 2-methyl-3-acetylquinoline (**4**) [*Anal.* Calc. for $C_{12}H_{11}NO$: C, 77.81; H, 5.97; N, 7.56. Found: C, 77.85; H, 5.99; N, 7.79%. δ_H $CDCl_3$: 2.42 (3H,s, CH_3), 2.67 (3H,s,$COCH_3$), 7.1–7.9 (4H,m,aromatic 5–8) and 8.22 (1H,s,aromatic 4); m.p. 77 ℃ (literature 74 ℃ [11], 78 ℃ [12]), semicarbazone m.p. 207 ℃ (literature 208 ℃ [12])]. The formation of the quinoline derivative **4** proceeded in two steps (Scheme 2), one of them being a Knoevenagel condensation between the carbonyl group of 2-aminobenzaldehyde and the reactive methylene group of pentane-2,4-dione catalyzed by strong basic properties of 1,2-diaminoethane. The presence of additional byproduct in the reaction mixture made the isolation of unsymmetrical ligand impossible.



2 1 3

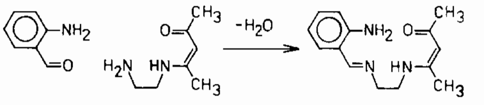
Scheme 1.



4

Scheme 2.

Otherwise, the reaction of 2-aminobenzaldehyde with the monocondensation product of pentane-2,4-dione and 1,2-diaminoethane (**5**) yielded unsymmetrical ligand (**6**) (Scheme 3). The FD mass spectrum of the reaction product contained only one intense peak at $m/z = 245$ corresponding to unsymmetrical compound **6**, but in spite of numerous attempts the ligand was not isolated in the crystalline form and was used for the preparation of metal complexes as crude oil.



5 6

Scheme 3.

We were not able to obtain the analogues of **6** wherein the aldehyde hydrogen atom would be replaced by methyl and phenyl groups. In the FD

TABLE I. Mass and Electronic Spectra of the Complexes

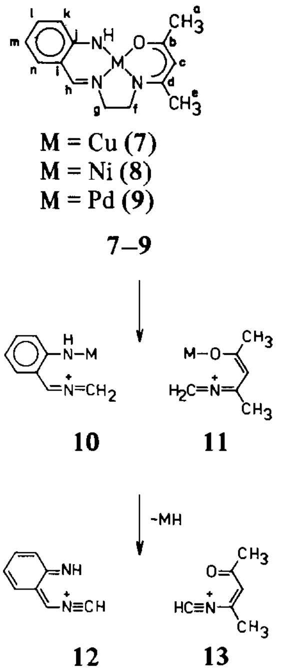
Compound	m/z[a]							λ_{max} (nm)[b]
	P^+	$[P\text{-}CH_3\dot{C}O]^+$	10	12	11	13	M^+	
7	306(100)	263(10)	195(12)	131(88)	174(67)	110(18)	63(10)	243(4.56), 325(3.95), 420(3.60), 500sh, 662(2.02)
8	301(100)	258(1)	190(9)	131(40)	169(35)		58(8)	238(4.26), 293(4.14), 412(3.48), 485(3.45)
9	349(43)		238(2)	131(100)	217(4)	110(19)	106(3)	

[a] m/z values are given for the most abundant isotopes with relative abundance (%) in parentheses, P denotes a parent (molecular) ion; [b] 10^{-3} mol dm^{-3} solution in methanol, values of log ϵ_{max} are given in parentheses.

mass spectra of reaction mixtures of 5 with 2-aminoacetophenone and 2-aminobenzophenone, peaks attributable to unsymmetrical ligands were not detected; the condensation did not occur. A similar decrease of reactivity towards primary amino groups of diamines by going from 2-aminobenzaldehyde to 2-aminoacetophenone and 2-aminobenzophenone had already been observed [13] and explained by steric hindrance exerted by the methyl and phenyl groups.

A considerable difference in the reactivity towards 5 between 2-amino- and 2-hydroxycarbonyl compounds may be explained by the lesser acidity of amine hydrogen atoms compared to that of the hydroxy group. The relatively high acidity of the phenolic hydrogen atom leads to the formation of intramolecular hydrogen bonding to the carbonyl oxygen atom and to increase of the partial positive charge on the carbonyl carbon atom, thus facilitating a nucleophilic attack of the primary amino-group of 5. In aminocarbonyl compounds, such a mode of intramolecular catalysis is far less efficient due to the very weak acidic properties of amine hydrogen atoms. For example, 2-hydroxybenzophenone reacted with the compound 5 forming quadridentate unsymmetrical ligand in good yield [1], whereas no trace of the corresponding 2-aminoderivative was detected in the reaction mixture of 2-aminobenzophenone and 5. Preliminary results of our further investigation confirm the influence of the acidity of the hydrogen atom involved in intramolecular bonding to the carbonyl oxygen atom upon the reactivity towards 5. An acylation of the amino-group enhances the acidic properties of the remaining amine hydrogen atom, and corresponding ligands are obtained in good yield.

The crude ligand 6 reacted readily with copper(II), nickel(II) and palladium(II) salts forming metal complexes 7, 8 and 9, respectively. In these complexes the metal ion is bound by the divalent anion resulting from the deprotonation of the enamine and aromatic amine groups of the ligand molecule. The presence of a single amine hydrogen atom in complexes gives rise to weak N–H stretching absorption bands at 3280 cm^{-1} (7), 3310 cm^{-1} (8) and 3330 cm^{-1} (9).



M = Cu (7)
M = Ni (8)
M = Pd (9)

7–9

10 11

12 13

Scheme 4.

In the mass spectra of the complexes (Table I), the molecular ion is of significantly greater abundance than other metal-containing ions and in the case of copper and nickel chelate gives rise to the base peak. The main fragmentation pathway (Scheme 4) involves the cleavage of the C–C bond in the ethylene bridge and simultaneous fission of two metal-donor bonds leading to the fragmentation ions 10 and 11 containing metal in the first oxidation state. Consequently, the fragments 10 and 11 eliminate the neutral molecule MH, forming organic ions 12 and 13. Generally, this fragmentation pathway is very similar to that found for symmetrical four-coordinated metal complexes [14], where the elimination of MH molecule from the fragmentation ions had been confirmed by the observation of

TABLE II. NMR Spectra[a] of Nickel and Palladium Complex

Compound		Methyl		Methylene		Methine		Aromatic		Other
		a	*e*	*f*	*g*	*c*	*h*	*k*	*m*	
8	δ_H[b]	1.870s[c]	1.811s	3.134t	3.420t	4.897s	7.420s	6.571db	6.166t	3.78br, 6.898t, 6.978db[d]
	δ_C[e]	24.4	21.3	51.5	60.1	99.8	161.2	114.7	121.9	176.1, 163.2, 115.6, 150.8, 131.4, 132.4[f]
9	δ_H[g]	1.990s	1.984s	3.477t	3.766t	4.888s	7.666s	6.662db	6.203t	5.49br, 7.016t, 7.082db[d]

[a] δ (ppm) in $CDCl_3$ solution with $SiMe_4$ as internal reference, s = singlet, db = doublet, t = triplet, br = broadened band; [b] 250 MHz spectrum; [c] the signal undergoes a larger $Eu(fod)_3$ induced shift than other methyl resonance. [d] resonances of protons: NH, *l* and *n* respectively; [e] proton decoupled spectrum; [f] resonances of carbons: *b, d, i, j, l* and/or *n*; [g] 360 MHz spectrum.

corresponding metastable ion. In the spectrum of the palladium complex (**9**), the abundance of ions **10** and **11** is considerably smaller than in the nickel and copper complexes, whereas the abundance of organic ions **12** and **13** is greater and the ion **12** is the base peak. The same effect was already observed for N_2O_2 analogues [8]. This phenomenon can be explained by the very strong affinity of palladium to hydrogen and by the relative facility of the palladium(II) ion to undergo reduction, both factors favouring the elimination of the PdH molecule.

In the electronic spectrum of the copper complex (**7**) (Table I) two absorption bands are observed in the visible region. One appears as a shoulder on the long-wave side of the intensive UV band. The second symmetrical band has a maximum at 662 nm in methanol, 653 nm in chloroform and 643 nm in acetone. Sensitivity of the lower-energy band position towards the nature of the solvent suggests that the band is associated with the $z^2 \rightarrow xy$ transition. Similar assignment of the lowest-energy band at 627 nm in the spectrum of a related copper complex 4,6,9-trimethyl-5,8-diazadodeca-3,9-diene-2,11-dionatocopper was made by Downing and Urbach [15] on the basis of circular dichroism studies. The EPR spectrum of the polycrystalline sample of the copper complex (**7**) is typical for an approximately axial system with $g_\parallel = 2.160$ and $g_\perp = 2.039$. In the perpendicular part of the EPR spectrum of this compound in frozen DMF solution (Fig. 1), seven lines of superhyperfine splitting, due to the interaction of electron spin with three ^{14}N nuclei, can be observed. It is interesting to note that the pattern is not obscured by the additional splitting with the azomethine hydrogen atom as in the case of related N_2O_2 copper complexes [9].

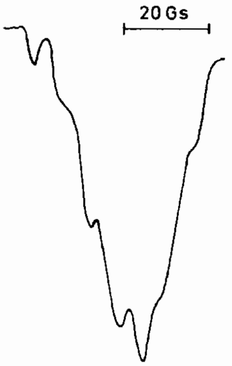


Fig. 1. The perpendicular part of the EPR spectrum of the copper complex (7) in frozen DMF solution at –130 °C.

Diamagnetism of the nickel complex (**8**) and lack of absorption above 1000 nm in its electronic spectrum as well as diamagnetism of palladium complex (**9**) are indicative of the square planar geometry of both complexes [16]. Their proton NMR spectra and ^{13}C NMR spectrum of **8** are given in Table II. Two singlets of methyl groups *a* and *e* in the proton NMR spectrum of compound **8** were distinguished by the observation of a shift of these resonances induced by the incremental addition of lanthanide shift reagent $Eu(fod)_3$, assuming the same mode of interaction as in the case of N_2O_2 analogues [1].

From the comparison of the proton NMR spectra of the complexes **8** and **9**, it is evident that in the case of the palladium chelate some resonances are shifted downfield as compared to the nickel complex. The largest shift of 1.71 ppm is observed for amine proton N$\underline{H}$ in α position; then the resonances of protons in β position *f, g, h* are shifted by about 0.3 ppm. For more distant protons the effect is negligible. This phenomenon, observed also for N_2O_2 complexes [1, 3, 8, 17], presumably arises from the difference in electronegativity of metals. Palladium is known to be more electronegative than nickel, their values of atomic electronegativity being 2.1 and 1.8, respectively [18].

References

1 E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta, 82,* 101 (1984).

2 G. Cros and J. P. Costes, *C.R. Acad. Sci. Paris, Ser. II, 294,* 173 (1982).

3 E. Kwiatkowski, M. Kwiatkowski and A. Olechnowicz, *Inorg. Chim. Acta, 90,* 145 (1984).
4 J. P. Costes, G. Cros, M. H. Darbieu and J. P. Laurent, *Inorg. Chim. Acta, 60,* 111 (1982); *Transition Met. Chem., 7,* 219 (1982).
5 J. P. Costes, G. Cros and J. P. Laurent, *Inorg. Chim. Acta, 97,* 211 (1985).
6 H. Adams, N. A. Bailey, I. S. Bard, D. E. Fenton, J. P. Costes, G. Cros and J. P. Laurent, *Inorg. Chim. Acta, 101,* 7 (1985).
7 L. J. Smith and W. J. Opie, *Org. Synth. Collect., 3,* 56 (1956).
8 E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta, 42,* 197 (1980).
9 H. A. Kuska, M. F. Farona, P. Pappas and S. Potterton, *J. Coord. Chem., 1,* 259 (1971).
10 H. P. Jensen, *Acta Chem. Scand., Ser. A, 36,* 825 (1982).
11 L. J. Eliasberg and P. Friedländer, *Chem. Ber., 25,* 1752 (1892).
12 O. Stark, *Chem. Ber., 40,* 3452 (1907).
13 M. Green and P. A. Tasker, *J. Chem. Soc. A,* 2531 (1970).
14 G. B. Westmore, in J. Charalombous (ed.), 'Mass Spectrometry of Metal Compounds', Butterworths, London, 1975, pp. 230–233.
15 R. S. Downing and F. L. Urbach, *J. Am. Chem. Soc., 91,* 5977 (1969).
16 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam, 1968, pp. 343, 349.
17 P. J. McCarthy and A. E. Martell, *Inorg. Chem., 6,* 781 (1967).
18 S. S. Bacanov, 'Elektrootracitelnost' Elementov', Izdatelstwo Akademii Nauk SSSR, Novosibirsk, 1962, p. 64.