Inorganica Chimica Acta, 41 (1980) 179–183
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Transition-metal Complexes of N-acetylpyrazole: Metal-ion Induced Enolisation

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Received January 2, 1980

A number of new coordination compound is reported with N-acetylpyrazole (acpz) as the ligand, viz. $M(acpz)Cl_2$ *with M is Mn, Co, and Cu,* $Ni(acpz)_2Cl_2$*, and* $[M(acpz)_3](BF_4)_2$ *with M is Mn, Fe, Co, Ni, Zn and Cd. In all compounds the ligand is chelated to the metal ion through the pyrazole nitrogen and the acetyl oxygen atoms, whereby in the case of the metal(II)fluoroborates the ligand exists in its enol form. These compounds must therefore be formulated as* $[M\{1\text{-}(1\text{-hydroxyethenyl})pyrazole\}_3](BF_4)_2$.

Introduction

The coordinating capacity of pyrazole was known as early as 1890 [1], but has been investigated extensively only recently [2]. One of the causes of the current interest being the biological implications of heterocyclic bases, at this laboratory, for some time, investigations have been going on on the complexing properties of small heterocyclic systems, including pyrazoles [3, 4], isoxazole [5] and triazoles [6]. As an extension of these studies, and because of the scanty material on mixed nitrogen-oxygen coordination, a study of the complexing properties of N-acetylpyrazole was taken up. In addition to the ring nitrogen as the donor atom, N-acetylpyrazole has the acetyl group in the 1-position to enable this compound to function as an 'endobidentate' ligand. Hitherto no complexes of N-acetylpyrazole are known, but from a similar compound, *viz.* 3,5-dimethyl-1-carbamoylpyrazole, a number of anionic complexes have been reported [7].

Experimental

The commercially available hexaquometal(II) fluoroborates, hydrated metal(II) chlorides, nitromethane, triethylorthoformate, and n-pentane were of sufficient purity. Nitromethane and n-pentane were dried with anhydrous calciumsulphate and sodium metal respectively. Anhydrous metal(II) chlorides were prepared by heating the hydrated metal(II) chlorides at 200 °C in a stream of dry HCl gas. N-acetylpyrazole was prepared from pyrazole and acetylchloride [8].

The N-acetylpyrazole–metal(II) fluoroborate solvates were prepared in the following way: a hexaquometal(II) bisfluoroborate (0.01 mol) was dissolved in excess triethylorthoformate (0.08 mol). After termination of the dehydration reaction most of the solvent was evaporated under reduced pressure. The almost dry residue was taken up in nitromethane. To this solution N-acetylpyrazole (0.03 mol) was added. After stirring it for several hours the resulting solution was concentrated by evaporation of nitromethane under reduced pressure and at slightly elevated temperature (50 °C). Upon cooling crystals separated. These were collected on a porous glass filter and washed with n-pentane. The solid compounds were evacuated for half an hour to remove remaining solvent or washing liquid. Attempts to obtain a magnesium(II) fluoroborate complex of N-acetylpyrazole were not successful.

The N-acetylpyrazole–metal(II) chloride adducts were synthesized by stirring an anhydrous metal(II) chloride (0.01 mol) and N-acetylpyrazole in nitromethane for twenty-four hours. Several metal to ligand ratios (1:1, 1:2, and 1:3) were tried. The resulting solid compound was collected on a porous glass filter and washed with n-pentane. Remaining solvent was removed by evacuation. No adducts with iron(II) chloride could be obtained as during the syntheses the ligand decomposed. Adducts of magnesium(II) chloride and of zinc(II) chloride and a solvate of copper(II) fluoroborate with reproducible stoichiometries could not be obtained.

Adducts with stoichiometries other than those listed in Table I were not obtained. Care was taken throughout to perform preparations and manipulations under anhydrous circumstances.

Reflectance spectra of the solid compounds were recorded in the visible and near infrared region on a Beckman DK-2 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer 580 spectrophoto-

TABLE I Metal(II) Complexes of N-acetylpyrazole (acpz) with Analytical Data (% weight), Melting Point (°C), and Colour

	Metal(II)		Chloride		Melting	
	calc	found	calc	found	point	colour
$Mn(acpz)Cl_2$	23 3	22 5	30 1	29 7	>300	white
$Co(acpz)Cl_2$	24 6	24 2	29 6	29 6	>300	blue
$Ni(acpz)_2Cl_2$	16 8	16 8	20 3	20 4	>300	yellow-green
$Cu(acpz)Cl_2$	26 0	25 9	29 0	28 7	190	green-yellow
$Mn(acpz)_3(BF_4)_2$	9 84	9 85			202	white
$Fe(acpz)_3(BF_4)_2$	9 98	9 94			167	beige-yellow
$Co(acpz)_3(BF_4)_2$	10 48	10 49			192	orange-red
$Ni(acpz)_3(BF_4)_2$	10 44	10 41			222	pale-blue
$Zn(acpz)_3(BF_4)_2$	11 49	11 48			90	white
$Cd(acpz)_3(BF_4)_2$	18 24	18 13			196	white

meter (4000–180 cm^{-1}) as nujol mulls between CsBr and polythene plates NMR-spectra were recorded on a Jeol JNM ps-100 apparatus as solutions in deuteronitromethane The metal contents were determined complexometrically, the chloride content was determined by the Volhard method

Results and discussion

General

In Table I ten coordination compounds of divalent transition metal ions with 1-acetylpyrazole as the ligand are listed with analytical data,colour and melting point From the stoichiometries and colours of the compounds it is clear already that the ligand functions as a bidentate oxygen-nitrogen donor ligand

The Infrared Spectrum of N-acetylpyrazole

Studies on the vibrational modes of N-acetylpyrazole apparently have not been performed, as any infrared spectral material on N-acetylpyrazole is lacking in the chemical literature Infrared assignments of pyrazole and of some substituted pyrazoles on the other hand have been reported [3, 9, 10], although not based on normal coordinate treatments By making use of these data a tentative assignment for N-acetylpyrazole has been set up (see Table II), based on the following considerations When comparing the infrared spectra of pyrazole and N-acetylpyrazole to each other, the similarity of large parts of these two spectra is striking Therefore most band assignments given in Table II have been taken over straightforwardly from the pyrazole band assignments The differences between the infrared spectra of pyrazole and N-acetylpyrazole are easily understood The absorption bands due to the N–H vibrations of pyrazole are not present in the spectrum of N-acetylpyrazole, while new bands have appeared obviously stemming from the acetyl group The very strong band at 1742 cm^{-1} is due of course to the carbonyl stretching vibration The 1417 cm^{-1} band is due probably to a C–H bending vibration of the acetyl group, because such bands occur in this region and because there are no indications that this band stems from another vibration mode The 1209 cm^{-1} band could be due either to the C–C or to the C–N stretching vibration of the substituent group It is very likely however that this band is due to the C–C stretching vibration, because the C–N stretching vibration, when it is present at all in the infrared spectra of such compounds, should occur at lower frequencies because of the large mass of the pyrazole entity (see also below at the infrared spectra of the metal(II)fluoborate complexes)

The 1337 cm^{-1} band is ascribed to a C–H bending vibration and the 1259 cm^{-1} band to a ring stretching vibration, although for pyrazole itself these assignments are reversed [3, 10] The reason for this interchange is, that upon complexing (see Table II) the 1337 cm^{-1} band is hardly shifted, while the 1259 cm^{-1} band shows quite large shifts [3, 5, 11]

Infrared Spectra of the Metal(II) chloride Complexes

In the metal(II) chloride adducts most of the infrared absorption bands of N-acetylpyrazole are shifted more or less with regard to the corresponding bands in the free ligand (see Table II) This generally occurring and well known phenomenon [3, 5, 11] denotes that bonding has taken place between the metal ion and the ligand The carbonyl stretching vibration shifts markedly to lower frequencies, which shows

TABLE II. Infrared Absorption Bands (cm^{-1}) of N-acetylpyrazole (acpz) and Its Adducts $M(acpz)Cl_2$ with M is Mn, Co, and Cu, and $Ni(acpz)_2Cl_2$.

acpz	Mn	Co	Ni	Cu	Assignment
3140 d, m-w[a]	3100	3110	3110	3110 d, m-w	ν_{C-H}
	2928	2930	2930	2928 m-w	ν_{C-H}
1742 vs	1704	1696	1696	1659 vs	$\nu C=O$
1546 m	1534	1534	1525	1539 m	νring
1417 m	1411	1407	1408	1407 m	δ_{C-H}
1387 s	1372	1377	1383	– s	ν_{ring}
1337 s	1338	1343	1344	1353 s	δ_{C-H}
1259 s	1292	1302	1298	1307 s	ν_{ring}
1209 s	1205	1213	–	1213 m	ν_{C-C}
1138 m	1074	1078	1120	1074 m	ring breathing
1040 m	1042	1053	1048	1046 m	δ_{C-H}
927 s	947	957	952	956 s	δ_{ring}
772 s	798	797	783	798 s	γ_{C-H}
643 s	663	663	666	672 m	δ_{ring}
615 m	601	602	597	599 m	δ_{ring}
	252	343	253	338 m	ν_{M-Cl}

[a] v = very, s = strong, m = medium, w = weak, d = doublet.

TABLE III. Infrared Absorption Bands (cm^{-1}) of the N-acetylpyrazole (acpz) Complexes $[M(acpz)_3](BF_4)_2$.

Mn	Fe	Co	Ni	Zn	Cd		Assignment
3405	3400	3395	3400	3360	3390	br, m[a]	ν_{O-H}
3150	3150	3150	3150	3150	3150	d, w	ν_{C-H}
2930	2930	2930	2930	2930	2930	w	ν_{C-H}
1529	1527	1528	1528	1540	1530	m	ν_{ring}
1477	1478	1475	1476	1490	1477	m	$\nu_{C=C}$
1404	1407	1406	1409	1410	1404	m	δ_{C-H}
1352	1356	1354	1358	1360	1352	m	δ_{C-H}
1293	1293	1294	1295	1290	1292	m-w	ν_{ring}
1050	1050	1050	1050	1050	1050	vbr, s	ν_{B-F}
914	914	913	915	913	912	m	δ_{ring}
874	873	875	877	875	872	m	see text
779	783	778	779	780	780	s	γ_{C-H}
688	687	688	690	695	685	s	δ_{ring}
593	593	599	602	602	590	s	δ_{ring}
524	526	524	526	523	532	m	δ_{B-F}
220	238	250	256	235	–	m	ν_{M-L}

[a] v = very, br = broad, s = strong, m = medium, w = weak, d = doublet.

[11, 12] that the ligand is bonded to the metal ions through the oxygen atom of the acetyl group. The ligand is also bonded to the metal ions through the N2 nitrogen atom of the pyrazole ring, because most of the vibrations involving the pyrazole ring have shifted to some extent [5], most shifts being even larger than corresponding shifts in complexes of pyrazole itself [3, 9].

In the far infrared region of all adducts one band appears which is not present in the infrared spectrum of the free ligand. We ascribe this band to the metal–chloride stretching vibration [13]. From the position of this band in these adducts it seems very likely that the manganese ions and the nickel ions are hexa-coordinated, while the cobalt ions and the copper ions are tetra-coordinated [13]. The ligand field spectra of the cobalt, nickel, and copper adducts support this assumption (see below).

Infrared spectra of the Metal(II) Fluoroborate Complexes

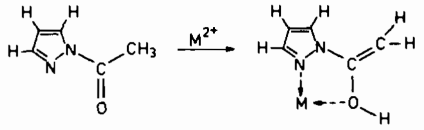
The infrared spectra of the N-acetylpyrazole–metal(II) fluoborate compounds are strongly different from the infrared spectrum of acetylpyrazole itself. The most striking differences are the disappearance of the strong absorption band due to the carbonyl stretching vibration and the appearance of a band around 3400 cm^{-1}. Also the 1209 cm^{-1} band has disappeared and a band around 1480 cm^{-1} and a band around 875 cm^{-1} are introduced. These results all point to a molecular rearrangement of the ligand N-acetylpyrazole, *i.e.* a transition of one of the methyl protons to the carbonyl oxygen. This implies that the carbonyl group, and thus the carbonyl stretching vibration (1742 cm^{-1}) disappears, that a hydroxyl group, and thus a hydroxyl stretching vibration (3400 cm^{-1}), is introduced, and that the single $C–CH_3$ bond of the acetyl group becomes a double $C=CH_2$ bond, which means the disappearance of the C–C stretching vibration (1209 cm^{-1}) and the appearance of a C=C stretching vibration (around 1480 cm^{-1}). The origine of the new band around 875 cm^{-1} in the complexes is less clearcut, as quite a variety of possible vibration modes arise, *e.g.* C–O or C–N stretching or C=C or O–H bending. The occurrence of anion vibrations at 1050 cm^{-1} and at about 525 cm^{-1}, and the absence of bands at 750 cm^{-1} and at 350 cm^{-1} make it clear that the tetrahedral BF_4^- anions are not bonded to the metal ions [3]. This implies that the metal(II) fluoborate complexes are true solvates [11], *i.e.* the divalent metal ions being coordinated solely by ligand molecules, which is affirmed by the ligand field spectra (see below).

The band in the 200–300 cm^{-1} region (see Table III) is assigned to the metal-ligand stretching vibration, because of its Irving–Williams behavior [5, 11, 12, 14].

The infrared spectra of the tris(N-acetylpyrazole)-metal(II)bisfluoroborate compounds all show the same pattern of bands and relative intensities, which means that these solid compounds are largely isomorphous.

NMR Spectra

The infrared data (*vide supra*) of the metal(II) fluoborate solvates point to the enolisation of 1-acetylpyrazole, upon complexing, to 1-(1-hydroxyethenyl)pyrazole:



To check this, proton NMR spectra were taken from 1-acetylpyrazole itself and from the diamagnetic zinc-fluoborate solvate of acetylpyrazole. The NMR spectrum of 1-acetylpyrazole shows four resonances at –2.64 ppm (singlet), –6.38 ppm (quartet), –7.66 ppm (singlet), and –8.21 ppm (doublet) from TMS. These signals are ascribed to the methyl protons of the acetyl group, and to the protons on the carbon atoms four, three, and five respectively from the shape, the position, and the area ratio (3:1:1:1) of the signals. These values are in good agreement to values reported by Elguero *et al.* [15]. The proton NMR spectrum of the zinc complex only showed signals at –6.69 ppm (singlet), at –8.07 ppm (singlet), and –10.61 ppm (broad singlet) from TMS, with an area ratio of 1.8:3:1.2. These data are indeed interpretable in terms of an enolised 1-acetylpyrazole compound, the signals being ascribable respectively to the two protons of the vinyl group, to the three pyrazole protons together, and to the hydroxyl proton.

Ligand Field Spectra

The reflectance spectrum of the iron(II) fluoborate solvate shows one asymmetrical band at 10950 cm^{-1} due to the $^5E_g \leftarrow {}^5T_{2g}$ transition. This band has definite doublet structure with a peak separation of about 1300 cm^{-1}, presumably due to a lower symmetry component (Jahn–Teller effect), which lifts the twofold degeneracy of the ^5E_g term [16]. The spectrum of the copper(II) fluoborate solvate consisted of one band at 18400 cm^{-1} with a shoulder at 15300 cm^{-1}, basically due to the $^2T_{2g} \leftarrow {}^2E_g$ transition, but the degeneracy of these levels being lifted apparently by a slight distortion (Jahn–Teller effect) of the octahedral symmetry. Shape and position of the bands of $Co(acpz)Cl_2$ are typical for tetrahedral coordination, the $^4T_1(F) \leftarrow {}^4A_2$ transition occurring at 6060 cm^{-1} and the $^4T_1(P) \leftarrow {}^4A_2$ transition at 14700 cm^{-1}. The reflectance spectrum of $Cu(acpz)Cl_2$ shows one asymmetrical band at 12650 cm^{-1}, indicating a tetragonal (square planar?) environment of the copper(II) ion.

The reflectance spectrum of $Ni(acpz)_2Cl_2$ resembles spectra of octahedral surrounded nickel(II) ions. Assignments of the bands and calculation of the ligand field parameters were therefore made accordingly [17, 18] (see Table IV). The value of Dq is very low, in accordance with the mixed coordination, *i.e.* two nitrogen, two oxygen, and two chloride atoms, of the nickel(II) ion. The low value of B also indicates that the crystal field environment of the metal ion deviates somewhat from octahedral

TABLE IV. Absorption Bands (cm^{-1}) of the Hexacoordinated Cobalt and Nickel Complexes in the Visible and Near Infrared Region with Their Assignments and Calculated Ligand Field Parameters.

$Co(acpz)_3(BF_4)_2$	9300	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	Dq = 1020 cm^{-1}
	20400	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	B = 820 cm^{-1}
$Ni(acpz)_3(BF_4)_2$	10300	$^3T_{2g} \leftarrow {}^3A_{2g}$	Dq = 1030 cm^{-1}
	16800	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	B = 840 cm^{-1}
	27000	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	
$Ni(acpz)_2Cl_2$	8600	$^3T_{2g} \leftarrow {}^3A_{2g}$	Dq = 860 cm^{-1}
	13900	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	B = 805 cm^{-1}
	23800	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	

symmetry. Shape and relative positions of the bands of the spectra of the cobalt(II) and nickel(II) fluoborate solvates are typical for octahedral coordination. Assignments of the bands and calculations of the ligand field parameters were made accordingly [17, 18] (see Table IV). The values of the spectrochemical parameter Dq appear to be rather low for nitrogen donor ligands and high for oxygen donor ligands [17, 18], as can be expected for a bidentate, mixed nitrogen–oxygen donor ligand.

Keto–Enol Tautomerism

It is a well known phenomenon that β-diketones and β-ketoesters participate in tautomeric equilibria, where an apparently pure compound is actually a mixture of two substances having keto and enol structures respectively [19]. The amounts of enol present in equilibrium with simple aliphatic monoketones, however, are very small, *e.g. ca.* 1 part in 10^6 for acetone [19]. The enolisation process for β-dicarbonyl compounds is exothermic and the stability of the enol form is increased relatively to the keto form by attaching an electron withdrawing group to one of the carbonyl carbon atoms or to the α-carbon atom [19]. The high position of the carbonyl stretching vibration of N-acetylpyrazole (1742 cm^{-1}) indicates that pyrazole acts as a rather strong electron withdrawing group [12, 20]. The electron withdrawing potential of the pyrazole entity is of course enhanced by the coordination of a metal ion to one of the pyrazole nitrogens. This may perhaps explain why N-acetylpyrazole is the first example of a monoketone that can be 'isolated' in its enol form. A certain stabilising effect of the coordinating metal ion on this ligand through the two metal–ligand bonds probably assists also.

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