MAGNETIC RESONANCE IN CHEMISTRY, VOL. 36, 279–284 (1998)

^{27}Al, ^{15}N, ^{13}C and ^{1}H NMR Spectra of the 2 : 1 Aluminium(III) Complexes of Some Azo Dyes

Antonín Lyčka,*† Paul Rys and Peter Skrabal

Laboratorium für Technische Chemie, Swiss Federal Institute of Technology (ETH), CH-8092 Zürich, Switzerland

Received 16 July 1997; revised 10 October 1997; accepted 25 October 1997

ABSTRACT: The ^{27}Al, ^{15}N, ^{13}C and ^{1}H NMR spectra in DMSO and ^{27}Al and ^{15}N magic angle spinning NMR spectra of 2:1 aluminium(III) complexes derived from 5-chloro-2-hydroxyaniline azo coupling products with acetoacetanilide, 3-methyl-1-phenylpyrazol-5-one and 2-naphthol were measured and analysed. It was found that the aluminium atom is six-coordinated, being bound to two oxygens and the nitrogen originating from 2-hydroxy-5-chloroaniline of each ligand, in an analogous fashion to 2:1 cobalt(III) complexes described earlier. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: aluminium(II)–azo dye complexes; ^{27}Al NMR; ^{15}N NMR; ^{13}C NMR; ^{1}H NMR; ^{15}N MAS NMR; ^{27}Al MAS NMR

INTRODUCTION

Metal–dye complexes play a very important role in dyestuff technology.[1–5] Chromium, cobalt, copper and nickel are used most frequently for these purposes.[1–5] More stringent government regulations tend to limit their use due to toxicological and ecological drawbacks of these colorants. There are trends now to replace the above-mentioned metals by less toxic ones, e.g. aluminium,[6] and to prepare environmentally safer dyes.

We have shown in previous papers[7,8] that NMR spectroscopy is a very sensitive probe for detecting small covalent modifications in diamagnetic coordination compounds. The aim of this work was to characterize some 2 : 1 aluminium(III) complexes of azo dyes (**1b**–**3b**; see Scheme 2) by means of ^{27}Al, ^{15}N, ^{13}C and ^{1}H NMR and also ^{27}Al and ^{15}N magic angle spinning (MAS) NMR spectra to study the structure from the viewpoint of coordination at the aluminium atom and to compare the data with those published for analogous complexes containing different metals.

EXPERIMENTAL

Synthesis

Sodium salts of compounds **1b**–**3b** (Scheme 2) were prepared from precursors **1a**–**3a** (Scheme 1) and $Al_2(SO_4)_3 \cdot 18\ H_2O$ analogously to cobalt derivatives in dimethylformamide (DMF) solution.[5] Compound **3b** was also prepared in an aqueous suspension according to a published procedure[6] (reaction time 16 h).

Compounds **1b**–**3b** were prepared ^{15}N labelled at N_b analogously in DMF solution[5] using $Na^{15}NO_2$ (95% ^{15}N) in the preparation of compounds **1a**–**3a**.

NMR Spectroscopy

The ^{27}Al (93.84 and 104.26 MHz), ^{15}N (36.50 and 50.69 MHz), ^{13}C (90.56 MHz) and ^{1}H (360.13 MHz) NMR spectra of compounds **1**–**3** were measured on Bruker AMX 360, AMX 400 and AMX 500 spectrometers in hexadeuterodimethyl sulfoxide (DMSO-d_6) at ambient temperature using a 5 mm broadband probe. The ^{27}Al chemical shifts are referred to external $Al(OH)_6^{3+}$ in water [$\delta(^{27}Al) = 0.0$], ^{15}N chemical shifts to external neat nitromethane [$\delta(^{15}N) = 0.0$] and ^{13}C and ^{1}H chemical shifts to the central peak of DMSO-d_6 [$\delta(^{13}C) = 39.60$, $\delta(^{1}H) = 2.55$]. Positive values of chemical shifts denote high-frequency shifts with respect to standards.

The ^{27}Al (104.26 MHz) and ^{15}N (40.56 MHz) MAS NMR spectra of compounds **1b**–**3b** in 4 mm zirconia rotors were measured on a Bruker AMX 400 spectrometer equipped with a multinuclear double-bearing probe. The high-power decoupling single-pulse sequence was applied with pulse width 2 μs (^{27}Al) and 5 μs (^{15}N), spectral width 21 034 Hz (^{27}Al) and 40 658 Hz (^{15}N), relaxation delay 3–20 s, spinning rate 4–8 kHz and 200–500 (^{27}Al) and 4000–8000 (^{15}N) scans. The ^{27}Al and ^{15}N chemical shifts are referred to the same absolute frequency of external $Al(OH)_6^{3+}$ and external nitromethane, respectively, as in solution NMR spectra.

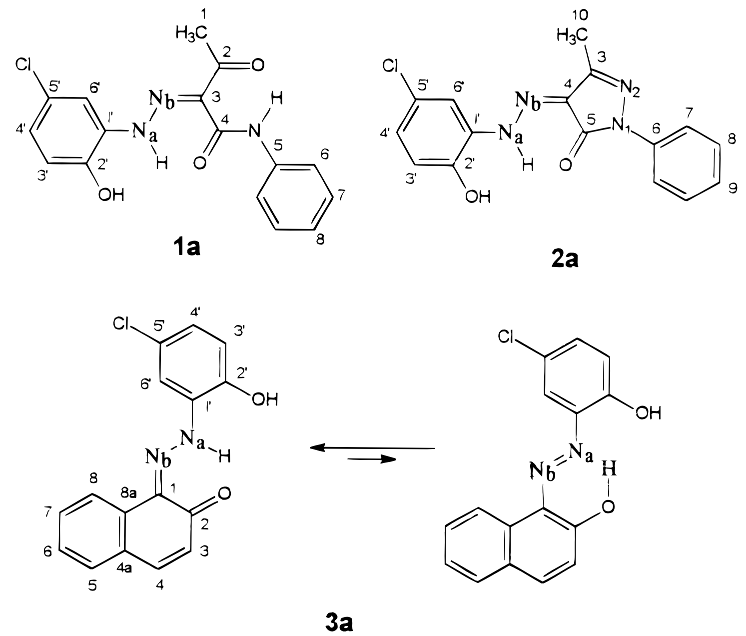
RESULTS AND DISCUSSION

The ^{27}Al, ^{15}N, ^{13}C and ^{1}H chemical shifts in ligands **1a**–**3a** and complexes **1b**–**3b** measured in DMSO-d_6 are given in Tables 1–3.

---

* *Correspondence to*: A. Lyčka, Research Institute for Organic Syntheses, CZ-532 18 Pardubice-Rybitvi, Czech Republic.
E-mail: slnmr@pol.upce.cz
† *Permanent address*: Research Institute for Organic Syntheses, CZ-532 18 Pardubice-Rybitvi, Czech Republic.

CCC 0749-1581/98/040279–06 $17.50



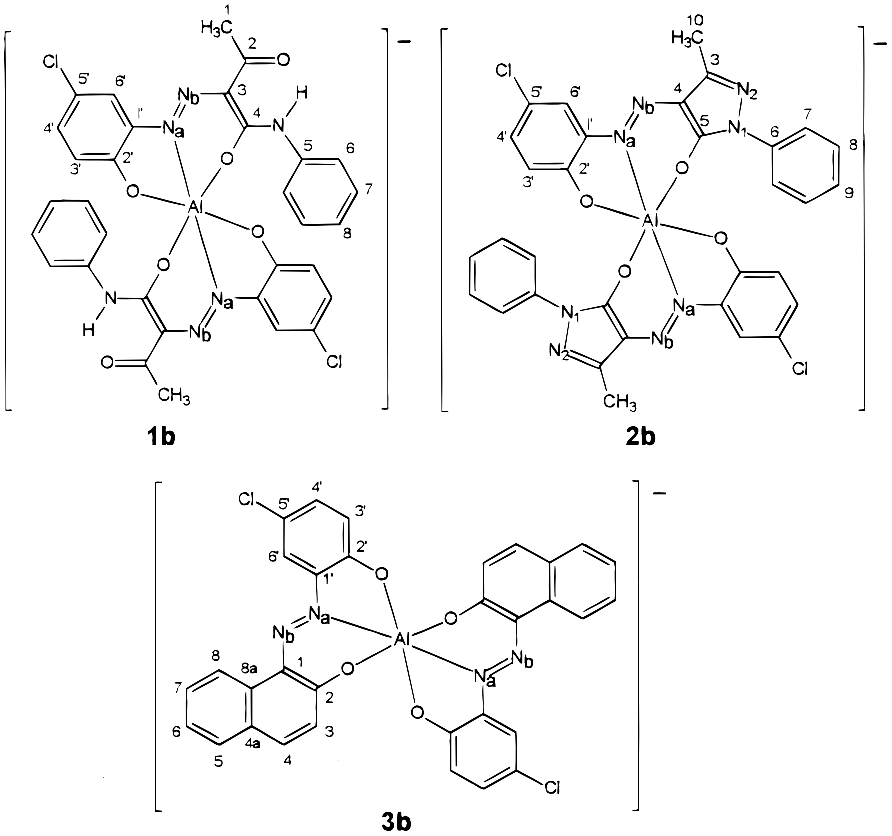
1a **2a** **3a**

Scheme 1.

The ^1H and ^{13}C chemical shifts were assigned using H,H-COSY, NOESY, H,C-COSY[9,10] [optimized for $^1J(^{13}C,H) \approx 150$ Hz and $^3J(^{13}C,H) \approx 8$ Hz], ^{13}C proton-coupled spectra and a comparison with published data.[7,8] Only one set of appropriate signals was obtained for compounds **1b**–**3b**, which means that the ligands are equivalent, at least on the NMR time-scale.

The same chemical shifts in DMSO solution within the experimental error were observed for samples of **3b** prepared both in DMF and in water.

The aluminium atom in 2:1 complexes **1b**–**3b** is expected to be four-coordinated.[6] This proposal is based on a common structural representation of simple aluminium compounds. However, these compounds can form dimers, trimers, tetramers and linear or cyclic polymers[11] and a coordination number of five or six has to be considered. Coordination of solvent molecules is another possibility to increase the coordination number of aluminium. In the case of **1b**–**3b**, the increase in coordination number might also be due to intramolecular bonding to one nitrogen of —N=N— or



1b **2b** **3b**

Scheme 2.

Table 1. ^{1}H, ^{13}C, ^{15}N and ^{27}Al NMR chemical shifts (δ, ppm) in compounds **1a** and **1b** in DMSO-d_6 and $^{n}J(^{15}N_b, ^{13}C)$ (Hz) in **1b**

	1a[a]		**1b**[b]		
Atom	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$^{n}J(^{15}N_b, ^{13}C)$
1	2.55	25.5	2.62	25.96	1.7
2	—	198.5	—	197.33	12.0
3	—	127.0	—	122.86	1.3
4	—	161.7	—	159.46	
NH	11.27	—	12.53	−251.2[c]	
5	—	136.8	—	136.48	
6	7.64	120.3	7.22	120.95	
7	7.40	128.7	7.14	128.92	
8	7.18	124.3	7.08	124.97	
1′	—	130.8	—	140.77	6.3
2′	10.60	144.9	—	157.97	2.7
3′	6.99	117.0	6.49	117.77	
4′	7.21	124.4	6.95	127.11	
5′	—	123.9	—	118.47	
6′	7.54	113.8	7.45	112.52	3.6
N_a	14.29	−210.8[c]	—	−103.2[c,d]	
N_b	—	−7.4[c]	—	46.8[c,d]	
				46.8[c,e]	
N_b (solid)	—	—	—	54.5[c,e]	
				49.6[c,e]	
Al	—	—	—	12.8[f]	
Al (solid)	—	—	—	6.6–8.6[f]	

[a] Data taken from Ref. 7.
[b] Prepared in DMF.
[c] $\delta(^{15}N)$.
[d] Measured at the natural abundance level of ^{15}N.
[e] ^{15}N-labelled compound.
[f] $\delta(^{27}Al)$.

—NHN= bonds per ligand.

^{27}Al NMR spectroscopy is a powerful tool for coordination number studies.[12–17] The ^{27}Al chemical shifts are determined by two main factors: coordination number and the nature of ligands. The ^{27}Al chemical shifts move generally more downfield on passing from six- to five- and four-coordinated aluminium atoms. There is usually a partial overlap between shift regions.[15] The ^{27}Al chemical shifts in compounds **1b**–**3b** were found to be in a very narrow range from 12.8 to 14.8 ppm outside the region of overlap and they give evidence for the aluminium central atom being six-coordinated. To decide if the sixfold coordination is due to solvent interaction (because DMSO is known to be a strong coordinating solvent) or to interaction with one nitrogen of each azo/hydrazone bond, a comparison of ^{27}Al chemical shifts measured in solution and in the solid state (i.e. without a strong coordinating solvent) is appropriate. ^{27}Al MAS NMR spectra of compounds **1b**–**3b** are shown in Fig. 1. The differences in ^{27}Al chemical shifts measured in DMSO solution and in the solid state are <10 ppm (the values of ^{27}Al MAS spectra being shifted upfield, i.e. in the direction of 'stronger' sixfold coordination). Therefore, we can exclude the coordination to DMSO and hence coordination via nitrogen is necessary.

The aluminium signals in the ^{27}Al MAS spectra show some indications of fine structure (Fig. 1). We can exclude the existence of residual ^{14}N quadrupolar coupling[18] because the signal patterns depend on the

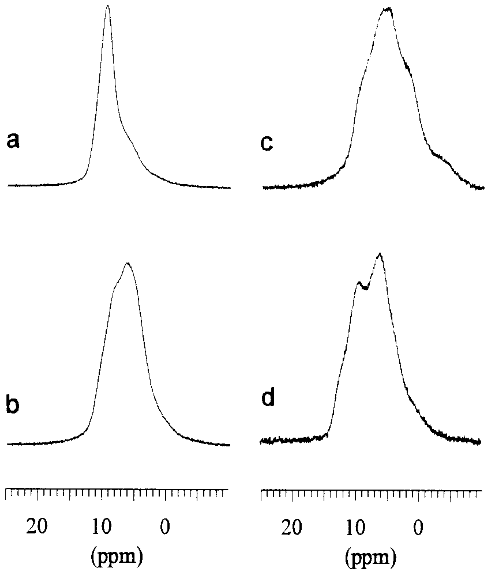


Figure 1. ^{27}Al MAS NMR spectra of compounds (a) **1b**, (b) **2b** and (c) **3b** prepared in DMF and (d) compound **3b** prepared in water.

Table 2. ^{1}H, ^{13}C, ^{15}N and ^{27}Al NMR chemical shifts (δ, ppm) in compounds **2a** and **2b** in DMSO-d$_6$ and $^{n}J(^{15}N_b, ^{13}C)$ (Hz) in **2b**

	2a		2b^{a}		
Atom	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$^{n}J(^{15}N_b, ^{13}C)$
3	—	148.95	—	148.44	8.1
4	—	128.81	—	124.56	2.6
5	—	156.96	—	150.82	
6	—	137.69	—	137.97	
7	7.93	117.48	7.61	119.13	
8	7.47	128.71	7.33	128.99	
9	7.25	124.70	7.16	125.41	
10	2.33	11.31	2.47	11.73	
1′	—	130.03	—	139.37	5.3
2′	10.83	144.89	—	158.99	2.9
3′	7.01	117.06	6.52	118.98	
4′	7.10	125.14	7.05	129.57	
5′	—	123.94	—	118.85	
6′	7.58	113.66	7.57	113.45	3.8
N_a	13.43	—	—	—	
N_b	—	$-26.0^{b,c}$	—	$37.7^{b,c}$	
N_b (solid)		—		$38.3^{b,c,d}$	
Al	—	—	—	14.8^{e}	
Al (solid)	—	—	—	6.6^{e}	

[a] Prepared in DMF.
[b] $\delta(^{15}N)$.
[c] ^{15}N-labelled compound.
[d] Broad signal.
[e] $\delta(^{27}Al)$.

Table 3. ^{1}H, ^{13}C, ^{15}N and ^{27}Al NMR chemical shifts (δ, ppm) in compounds **3a** and **3b** in DMSO-d$_6$ and $^{n}J(^{15}N_b, ^{13}C)$ (Hz) in **3b**

	3a		3b^{a}		
Atom	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$^{n}J(^{15}N_b, ^{13}C)$
1	—	130.18	—	130.45	
2	—	174.97	—	158.27	
3	6.80	125.54	6.73	125.52	
4	7.91	141.20	7.81	137.29	
4a	—	127.81	—	126.50	
5	7.73	129.04	7.78	128.22	
6	7.45	126.35	7.39	123.47	
7	7.61	129.37	7.65	128.12	
8	8.50	121.68	8.75	120.76	
8a	—	132.79	—	134.08	8.2
1′	—	132.21	—	140.44	4.9
2′	10.97	147.01	—	160.64	2.8
3′	7.05	117.59	6.52	119.63	
4′	7.21	126.85	7.14	131.15	
5′	—	124.35	—	118.98	
6′	7.91	115.04	7.84	114.33	3.8
N_a	16.22	-156.9^{b}	—	—	
N_b	—	-1.5^{b}	—	$50.8^{b,c}$	
N_b (solid)	—	—	—	$54.0^{b,c}$	
Al	—	—	—	13.3^{d}	
Al (solid)	—	—		$6.3–9.4^{d}$	

[a] Prepared in DMF.
[b] $\delta(^{15}N)$.
[c] ^{15}N-labelled compound.
[d] $\delta(^{27}Al)$.

method of preparation, as shown in Fig. 1(c) and (d) for samples of **3b** prepared in DMF and water, respectively. We believe that the fine structure is possibly due to the existence of crystal modifications, different microcrystallinity or polymorphism.[19]

Lehmann and Rihs have shown,[20] using x-ray methods, that all three possible isomers (N_a/N_a, N_a/N_b and N_b/N_b) can exist in 2:1 azo metal (Cr, Co) complex dyes and demonstrated that N_b coordination is kinetically favoured over N_a coordination while the N_b/N_b isomer is thermodynamically the most stable isomer. The reaction time and conditions can be of great importance for the properties (shade, strength, stability, etc.) of azo–metal complex dyes.

As discussed above, coordination via nitrogen is most likely in compounds **1b**–**3b**. Additional indications come from ^{15}N NMR spectra. In a previous paper,[7] we reported on the application of ^{15}N NMR as a very sensitive technique for the detection of the existence of coordination and for the determination of the coordination position of the nitrogen atoms in —N=N— and —NHN= groups.

Upfield ^{15}N chemical shifts of about 100 ppm have been observed on protonation of various heterocyclic derivatives, e.g. pyridine, purine, indolizine, etc.,[21,22] where the nitrogen atom lone pairs are engaged in bonding. A similar effect [$\Delta\delta(^{15}N) = 102–146$ ppm][23] is also typical of the coordination of a nitrogen atom of azo dyes, provided that the dyes exist in the azo form. On the other hand, coordination can cause a relatively large downfield shift when a ligand exists in the hydrazone form and changes in $\delta(^{15}N)$ are due to a combination of two effects: the coordination (responsible for an upfield shift) and the change of the hydrazone tautomeric form to the azo form (responsible for even greater downfield shift). Details have been published previously.[7]

We measured the ^{15}N chemical shifts of **1b**, which is the most soluble compound, at the natural abundance level and in $^{15}N_b$ enriched (95% ^{15}N) compounds **1b**–**3b**. In the cobalt(III) analogue[7] of **1b**, which is known to have a sixfold coordinated central cobalt atom, the ^{15}N chemical shifts found in DMSO-d_6 were $\delta(^{15}N_a) = -113.7$ and $\delta(^{15}N_b) = 46.3$. Very similar ^{15}N chemical shifts were measured in compounds **1b**–**3b**, giving evidence for N_a coordination.[7] The difference in $\delta(^{15}N_b)$ in **1b**–**3b** measured in solution and the solid state is very small (Tables 1–3). Two well separated signals were observed in the solid state in **1b** [$\delta(^{15}N_b) = 54.5$ and 49.6; see Fig. 2], whereas only one slightly broadened signal was found in **3b**. Compound **2b** gives a broad signal at *ca.* 38.3 ppm, showing 'fine' structure when line narrowing was applied.

Different changes in the ^{15}N chemical shifts of compounds **1b**–**3b** (Tables 1–3) compared with the values for ligands **1a**–**3a** are caused by the fact that **1a** and **2a** exist completely in the hydrazone form whereas in **3a** the hydrazone content can be estimated to be *ca.* 75%.[24]

$^2J(^{15}N,^{13}C)$ coupling constants are known to show stereospecific behaviour.[25] Carbon atoms in a *cis* position to the nitrogen lone pair give $^2J(^{15}N,^{13}C)$ coupling constants of about 8–13 Hz in planar model compounds whereas those in a *trans* position to the nitrogen lone pair have $^2J(^{15}N,^{13}C)$ coupling constants close to zero. These coupling constants are affected especially by the electronegativities of substituents (and also by other effects), but their difference is always significant.

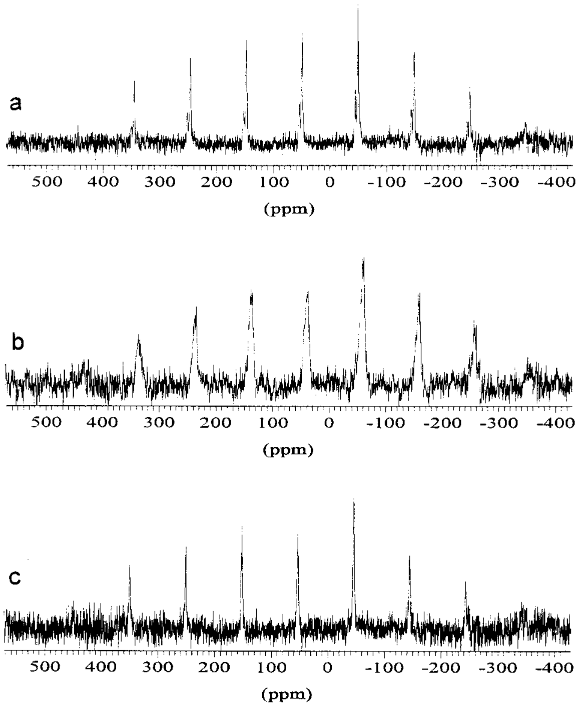
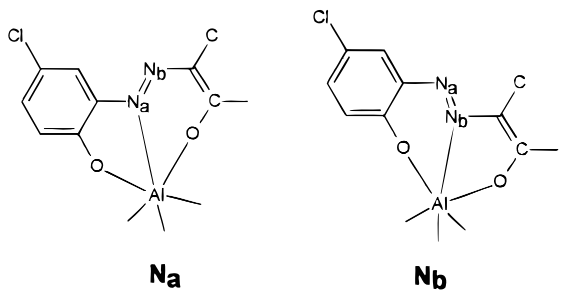


Figure 2. ^{15}N MAS NMR spectra of $^{15}N_b$-enriched compounds (a) **1b**, (b) **2b** and (c) **3b** prepared in DMF.

In ligands **2a** and **3a**, there is only one oxygen atom in the pyrazolone or naphthol parts of the molecules capable of complexing aluminium. The respective parts in the complexes are rigid and the $^2J(^{15}N_b,^{13}C)$ coupling constants can be used as an additional and independent proof of N_a *vs.* N_b isomerism. We found that the $^2J(^{15}N_b,^{13}C)$ coupling constant of C-3 in the pyrazolone ring of **2b** is 8.1 Hz and the signals of the C=O group of the pyrazolone ring gave no splitting. Similarly, the $^2J(^{15}N_b,^{13}C)$ coupling constant of C-8a is 8.2 Hz and no splitting was found for C-2. Such a situation can only exist in N_a isomers in which the N_b lone pair is in a *cis* position with respect to C-3 in **2b** and C-8a in **3b** (Scheme 3).

In ligand **1a**, there are two oxygens [—C(=O)— and —CONH—] in the acetoacetanilide part of the mol-



Scheme 3.

ecule capable of complexing aluminium. The complexation of metals via the —C(=O)— oxygen has been reported.[1–6] According to the ^{15}N chemical shifts, similar to those in **2b** and **3b**, compound **1b** is the N_a isomer. $^2J(^{15}N_b, ^{13}C)$ is 12.0 Hz for C-2 and <1 Hz for C-4, giving evidence that, similarly to the cobalt analogue,[7] the aluminium is bound to oxygen originating from the amide group in **1b** and not to the oxygen from the $COCH_3$ group as usually reported.[6]

The differences in the ^1H and ^{13}C chemical shifts in **1b**–**3b** compared with analogous Co complexes[7] can be ascribed to changes in bond lengths and bond angles due to the different radius of the central atom. Analogous changes were observed for nickel and platinum complexes of the same ligands.[8]

Acknowledgements

The authors thank Mr M. Lauwiner for skilful technical assistance and Mr. F. Bangerter for recording most of the NMR spectra.

REFERENCES

1. R. Price, in *The Chemistry of Synthetic Dyes*, edited by K. Venkataraman, Vol. III, Chapt. VII. Academic Press, New York (1970).
2. H. Baumann, in *Ullmanns Encyclopaedie der Technischen Chemie*, Vol. 16. Verlag Chemie, Weinheim (1978).
3. F. Beffa and G. Back, *Rev. Prog. Color. Relat. Top.* **14**, 33 (1984).
4. H. Zollinger, *Color Chemistry. Syntheses, Properties and Application of Organic Dyes and Pigments.* Verlag Chemie, Weinheim (1987).
5. K.-H. Schündehüte, in *Methoden der Organischen Chemie* (*Houben–Weyl*), edited by R. Stroh, Vol. 10/3. Georg Thieme, Stuttgart (1965).
6. B. L. Kaul and D. Pflieger, *Br. Pat.* 2 259 305 A (1993).
7. A. Lyčka, J. Jirman and A. Cee, *Magn. Reson. Chem.* **28**, 408 (1990).
8. J. Abilgaard, P. E. Hansen, J. Josephsen and A. Lyčka, *Inorg. Chem.* **33**, 5271 (1994).
9. R. R. Ernst, G. Bodenhausen and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions.* Clarendon Press, Oxford (1987).
10. W. Hull, in *Two-Dimensional NMR Spectroscopy. Application for Chemists and Biochemists*, edited by W. R. Croasmun and R. M. K. Carlson, 2nd ed., Chap. 2. VCH, New York (1994).
11. O. Kříž, B. Čásenský, A. Lyčka, J. Fusek and S. Heřmánek, *J. Magn. Reson.* **60**, 375 (1984).
12. J. W. Akitt, *Annu. Rep. NMR Spectrosc.* **5A**, 465 (1972).
13. J. F. Hinton and R. W. Briggs, in *NMR and the Periodic Table*, edited by R. K. Harris and B. E. Man, p. 259. Academic Press, London (1978).
14. J.-J. Delpuech, in *NMR of Newly Accessible Nuclei*, edited by P. Laszlo, Vol. 2, p. 153. Academic Press, New York (1983).
15. J. W. Akitt, in *Multinuclear NMR*, edited by J. Mason, Chapt. 9. Plenum Press, New York (1987).
16. J. W. Akitt, *Prog. Nucl. Magn. Reson. Spectrosc.* **21**, 1 (1989).
17. A. B. P. Lever (Ed.), *Coord. Chem. Rev.* **149**, 1–400 (1996).
18. R. K. Harris and A. C. Olivieri, *Prog. Nucl. Magn. Reson. Spectrosc.* **24**, 435 (1992).
19. G. McGeorge, R. K. Harris, A. M. Chippendale and J. F. Bullock, *J. Chem. Soc., Perkin Trans.* 2 1733 (1996).
20. U. Lehmann and G. Rihs, in *Chemistry of Functional Dyes*, edited by Z. Yoshida and T. Kitao, p. 215. Mita Press, Tokyo (1989).
21. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.* **25**, 57 (1993).
22. J. W. Wiench, L. Stefaniak and G. A. Webb, *Magn. Reson. Chem.* **32**, 373 (1994).
23. L. Tušek-Božič, M. Ćurič, D. Vikič-Topič and A. Lyčka, *Collect. Czech. Chem. Commun.* **62**, 1888 (1997).
24. A. Lyčka, *Annu. Rep. NMR Spectrosc.* **26**, 247 (1993).
25. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.* **18**, 195 (1986).