Orbett T. Alexander* and Andreas Roodt

The crystal structure of (*E*)-1-(quinolin-2-ylmethyl)-2-((1-(quinolin-2-ylmethyl)pyridin-2(1*H*)-ylidene)amino)pyridin-1-ium, C₃₀H₂₅BrN₅

<https://doi.org/10.1515/ncrs-2020-0323>

Received July 1, 2020; accepted July 17, 2020; available online August 7, 2020

Abstract

$\text{C}_{30}\text{H}_{25}\text{BrN}_5$, monoclinic, $P2_1/c$ (no. 14), $a = 15.685(4)$ Å, $b = 9.317(2)$ Å, $c = 18.373(4)$ Å, $\beta = 114.422(7)^\circ$, $V = 2444.8(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0377$, $wR_{\text{ref}}(F^2) = 0.0849$, $T = 112(2)$ K.

CCDC no.: 1985437

The molecular structure is shown in the figure (All the H-atoms on the title structure were omitted for clarity.). Table 1 contains crystallographic data and Table 2 contains the list

***Corresponding author: Orbett T. Alexander**, Department of Chemistry, University of the Free State, Bloemfontein 9301, South Africa, e-mail: alexanderorbett@gmail.com. <https://orcid.org/0000-0003-4926-8342>

Andreas Roodt: Department of Chemistry, University of the Free State, Bloemfontein 9301, South Africa

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.30 \times 0.26 \times 0.14$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.71 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	53790, 6124, 0.089
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4885
$N(\text{param})_{\text{refined}}$:	325
Programs:	Bruker [1], SIR97 [2], Olex2 [3], SHELXL [4], Diamond [5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	−0.11227(2)	0.70864(2)	0.05024(2)	0.02269(7)
N1	0.14419(12)	0.62501(19)	0.25912(10)	0.0188(4)
N1A	0.18636(12)	0.46520(18)	0.18497(10)	0.0165(4)
N1B	0.10055(12)	0.79117(19)	0.32896(10)	0.0175(4)
N2A	0.29194(13)	0.68766(19)	0.15754(10)	0.0188(4)
N2B	0.32601(12)	0.92018(19)	0.34412(11)	0.0186(4)
C1A	0.17776(14)	0.4953(2)	0.25470(12)	0.0174(4)
C1B	0.09757(14)	0.6516(2)	0.30372(12)	0.0166(4)
C2A	0.21108(15)	0.3895(2)	0.31570(13)	0.0210(4)
H2A	0.205685	0.405126	0.364721	0.025*
C2B	0.04205(15)	0.5551(2)	0.32527(13)	0.0220(5)
H2B	0.038442	0.457157	0.309843	0.026*
C3A	0.25054(16)	0.2661(2)	0.30488(13)	0.0230(5)
H3A	0.271569	0.195782	0.345970	0.028*
C3B	−0.00625(16)	0.6010(3)	0.36785(14)	0.0250(5)
H3B	−0.043080	0.534753	0.381797	0.030*
C4A	0.26047(16)	0.2420(2)	0.23331(14)	0.0229(5)
H4A	0.289220	0.156746	0.225948	0.027*
C4B	−0.00208(16)	0.7452(3)	0.39128(13)	0.0236(5)
H4B	−0.036209	0.777502	0.420487	0.028*
C5A	0.22809(15)	0.3429(2)	0.17484(13)	0.0211(4)
H5A	0.234604	0.328223	0.126221	0.025*
C5B	0.05162(15)	0.8372(2)	0.37136(13)	0.0212(5)
H5B	0.055399	0.934975	0.387023	0.025*
C6A	0.14321(15)	0.5639(2)	0.11704(12)	0.0197(4)
H6AA	0.081131	0.593569	0.113823	0.024*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H6AB	0.133006	0.511918	0.067126	0.024*
C6B	0.16514(14)	0.8914(2)	0.31576(13)	0.0197(4)
H6BA	0.151769	0.990164	0.327953	0.024*
H6BB	0.154360	0.888295	0.258749	0.024*
C7A	0.20035(15)	0.6965(2)	0.12195(12)	0.0178(4)
C7B	0.26658(15)	0.8560(2)	0.36704(12)	0.0177(4)
C8A	0.15131(16)	0.8212(2)	0.08241(13)	0.0224(5)
H8A	0.084818	0.823177	0.060157	0.027*
C8B	0.29345(16)	0.7650(2)	0.43421(13)	0.0225(5)
H8B	0.247609	0.722206	0.448572	0.027*
C9A	0.20005(16)	0.9381(2)	0.07651(14)	0.0242(5)
H9A	0.168246	1.021575	0.048878	0.029*
C9B	0.38617(16)	0.7396(3)	0.47809(13)	0.0247(5)
H9B	0.405774	0.676987	0.522860	0.030*
C10A	0.29913(16)	0.9328(2)	0.11239(13)	0.0202(4)
C10B	0.45289(15)	0.8069(2)	0.45658(12)	0.0207(4)
C11A	0.34227(15)	0.8062(2)	0.15418(12)	0.0189(4)
C11B	0.41949(15)	0.8973(2)	0.38887(13)	0.0182(4)
C12A	0.44089(16)	0.7999(2)	0.19148(13)	0.0228(5)
H12A	0.470803	0.716443	0.220531	0.027*
C12B	0.48420(16)	0.9670(2)	0.36622(14)	0.0243(5)
H12B	0.462293	1.027464	0.320489	0.029*
C13A	0.49393(16)	0.9127(3)	0.18627(13)	0.0255(5)
H13A	0.560288	0.906874	0.211712	0.031*
C13B	0.57827(17)	0.9488(3)	0.40922(15)	0.0266(5)
H13B	0.621229	0.996306	0.393120	0.032*
C14A	0.45106(17)	1.0371(3)	0.14361(14)	0.0264(5)
H14A	0.488522	1.114301	0.139704	0.032*
C14B	0.61185(16)	0.8601(3)	0.47717(15)	0.0270(5)
H14B	0.677387	0.848841	0.507070	0.032*
C15A	0.35572(17)	1.0474(2)	0.10773(14)	0.0253(5)
H15A	0.327207	1.132267	0.079446	0.030*
C15B	0.55092(16)	0.7899(3)	0.50048(13)	0.0249(5)
H15B	0.574196	0.729528	0.546229	0.030*

of the atoms including atomic coordinates and displacement parameters.

Source of material

To a stirred solution of 2,2''-dipyridylamine (0.2004 g, 1.168 mmol) in 15 mL of THF, a solution of KOH (0.655 g, 1.168 mmol) in water (10 mL) was added drop-wise. The solution was left to stir overnight. Later, 15 mL of THF solution of 2-(bromomethyl)-quinoline (0.2601 g, 1.168 mmol) was added drop-wise with stirring at room temperature. Stirring was continued overnight after which white precipitates formed and filtered off and washed with water and cold THF. The colourless salt product crystals fell-off in the water/THF filtrate.

¹H NMR (400 MHz, CDCl₃) δ 7.99 (dd, *J* = 6.6, 1.1 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.84–7.77 (m, 2H), 7.68–7.62 (m, 1H), 7.61–7.52 (m, 2H), 7.24 (d, *J* = 8.9 Hz, 1H), 6.87 (td, *J* = 6.9,

1.3 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.90 (s), 143.24 (s), 137.76 (s), 130.85 (s), 129.54 (s), 128.82 (s), 128.18 (s), 127.63 (s), 120.02 (s), 118.31 (s), 117.10 (s), 114.38 (s).

Experimental details

The aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95 and 0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) and 1.2*U*_{eq}(C), respectively. The placement of the H atoms of the methylene group were fixed (HFIX 23). The graphics were obtained using the DIAMOND program with 50% probability ellipsoids.

Comment

Organic ligand designing has been a useful tool for many centuries and have shown successful milestone to date [6, 7]. This practice is often an attempt to alter and/or improve the chemical properties of the ligand; be it the electronic or steric properties [8]. Pyridyl based type of ligands have contributed a great deal across many fields [9–12]. Subsequently, a great deal of interest towards multi-dentate pyridyl based ligands has grown over the decades across many disciplines including photoluminescence [13], medicinal chemistry [14], catalysis [15, 16] and radiopharmaceutical [17] chemistry, also as pursued in our research group [18–20]. It is for this evidence that the tailoring of the multi-dentate ligands are still of paramount importance.

There is one molecule in the asymmetric unit cell of the title structure. The crystal structure is symmetric in solution with N1 as the bridging imino nitrogen atom in the ligand. The cationic ligand crystallized with a bromide anion to balance the charge of the quaternary ammonium group (N1a/N1b). No protons on the bridging N-atom were detected, thus, to balance the charges (one bromide counterion clearly observed), an imino bridging entity was concluded [21]. The crystal structure is stabilized by very weak intra and inter-molecular hydrogen bonding interactions between Br1 and hydrogen atoms from neighbouring molecules. The conformation of the cation has the aromatic rings orientated in such a way that *pi-pi* packing is not favoured.

Acknowledgements: The authors would like to express their gratitude towards the University of the Free State for financial support.

References

1. Bruker. SAINT-Plus (version 7.12) and SADABS (Version 2004/1). Bruker AXS Inc., Madison, WI, USA (2004).
2. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.;

- Polidori, G.; Spagna, R.: A new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **32** (1999) 115–119.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42** (2009) 339–341.
4. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
5. Brandenbug, K.; Putz, H.: DIAMOND. Visual crystal structure information system. Ver. 3.0c Crystal Impact GbR, Bonn, Germany (2005).
6. Li, G.; Qian, X.; Cui, J.; Huang, Q.; Zhang, R.; Guan, H.: Synthesis and herbicidal activity of novel 3-aminocarbonyl-2-oxazolidinethione derivatives containing a substituted pyridine ring. *J. Agric. Food Chem.* **54** (2006) 125–129.
7. Wachter, G. A.; Davis, M. C.; Martin, A. R.; Franzblau, S. G.: Antimycobacterial activity of substituted isosteres of pyridine- and pyrazinecarboxylic acids. *J. Med. Chem.* **41** (1998) 2436–2438.
8. Matos, M. J. B.; Pina, A. S.; Roque, A. C. A.: Rational design of affinity ligands for bioseparation. *J. Chromatogr. A* **1619** (2020) 460871–460884.
9. Van der Westhuizen, H. J.; Meijboom, R.; Schutte, M.; Roodt, A.: Mechanism for the formation of substituted manganese(V) cyanidonitrido complexes: crystallographic and kinetic study of the substitution reactions of *trans*-[Mn(H₂O)(CN)₄]²⁻ with monodentate pyridine and bidentate pyridine-carboxylate ligands. *Inorg. Chem.* **49** (2010) 9599–9608.
10. Simmonds, H. R.; Wright, D. S.: Main group pyridyl-based ligands; strategies to mixed metal complexes. *Chem. Commun.* **48** (2012) 8617–8624.
11. Roy, S.; Colombo, E.; Vinck, R.; Mari, C.; Rubbiani, R.; Patra, M.; Gasser, G.: Increased lipophilicity of halogenated ruthenium(II) polypyridyl complexes leads to decreased phototoxicity in vitro when used as photosensitizers for photodynamic therapy. *ChemBioChem* (2020) <https://doi.org/10.1002/cbic.202000289>.
12. Karges, J.; Heinemann, F.; Jakubaszek, M.; Maschietto, F.; Subecz, C.; Dotou, M.; Vinck, R.; Blacque, O.; Tharaud, M.; Goud, B.; Viñuelas Zahínos, E.; Spingler, B.; Ciofini, I.; Gasser, G.: Rationally designed long-wavelength absorbing Ru(II) polypyridyl complexes as photosensitizers for photodynamic therapy. *J. Am. Chem. Soc.* **142** (2020) 6578–6587.
13. Koshevoy, I. O.; Krause, M.; Klein, A.: Non-covalent intramolecular interactions through ligand-design promoting efficient photoluminescence from transition metal complexes. *Coord. Chem. Rev.* **405** (2020) 213094–213110.
14. Martín, J.; Alés, M. R.; Asuero, A. G.: An overview on ligands of therapeutically interest. *Pharm. Pharmacol. Int. J.* **6** (2018) 198–214.
15. Choy, Y. P.; He, X.; Kwong, F. Y.: *Palladacycles: catalysis and beyond*. Elsevier B. V., Amsterdam, Netherlands (2019).
16. Queyriaux, N.; Jane, R. T.; Massin, J.; Artero, V.; Chavarot-Kerlidou, M.: Recent developments in hydrogen evolving molecular cobalt(II)–polypyridyl catalysts. *Coord. Chem. Rev.* **304** (2015) 3–19.
17. Volkert, W. A.; Hoffman, T. J.: Therapeutic radiopharmaceuticals. *Chem. Rev.* **99** (1999) 2269–2292.
18. Warsink, S.; Kotze, P. D. R.; Janse van Rensburg, J. M.; Venter, J. A.; Otto, S.; Botha, E.; Roodt, A.: Kinetic-mechanistic and solid-state study of the oxidative addition and migratory insertion of iodomethane to [rhodium(*S,O*-BdiPT or *N,O*-ox)(CO)(PR¹R²R³)] complexes. *Eur. J. Inorg. Chem.* **32** (2018) 3615–3625.
19. Brink, A.; Kroon, R. E.; Visser, H. G.; van Rensburg, C. E. J.; Roodt, A.: Designing model imino bifunctional chelators for radiopharmaceuticals—in vitro antitumor activity, photoluminescence and structural analysis. *New J. Chem.* **42** (2018) 5193–5203.
20. Frei, A.; Mokolokolo, P. P.; Bolliger, R.; Braband, H.; Tsosane, M. S.; Brink, A.; Roodt, A.; Alberto, R.: Self-assembled multinuclear complexes incorporating Tc-99m. *Chem. Eur. J.* **24** (2018) 10397–10402.
21. Kim, C.; Kim, Y.: CCDC 861315: experimental crystal structure determination, 2016, DOI: 10.5517/ccxx8cf.